Probing Thermosalience in Guanidinium Nitrate

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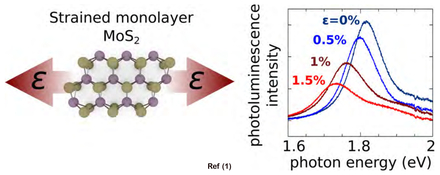
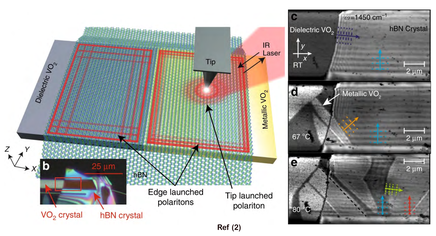
Active Tuning with Phase Change Materials

Straining low dimensional materials has been shown to actively tune both phonon modes and other optical properties of materials.



Ref (1)

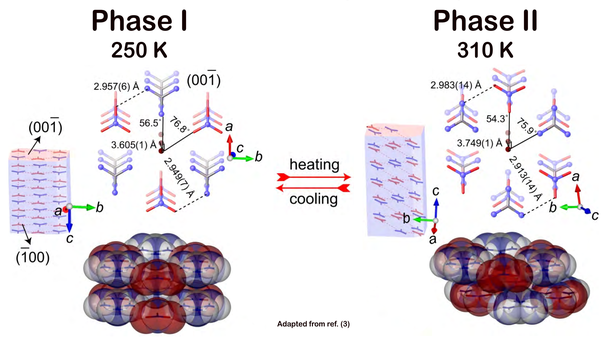
By using phase change materials (PCMs) we can dynamically modulate both local strain and dielectric environment for active tuning of optical responses, such as hyperbolic phonon polariton dispersion.



Ref (2)

GN Phase Transition

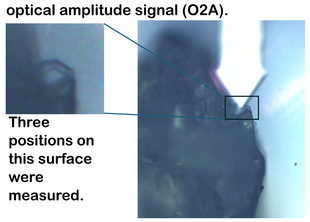
Guanidinium nitrate (GN) undergoes the largest reversible mechanical deformation, up to 51% expansion.



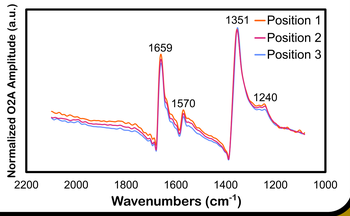
Adapted from ref. (3)

Previous Work from Our Group

Our group has used Nano-FTIR, which employs scattering-type scanning near-field optical microscopy (s-SNOM), to study GN previously and identified several peaks of interest in the warm phase of GN. Best signal to noise ratio was observed in the second harmonic optical amplitude signal (O2A).

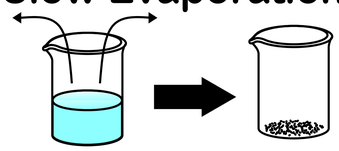


Three positions on this surface were measured.

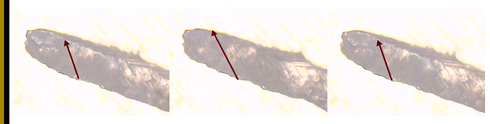


Crystallization Methods

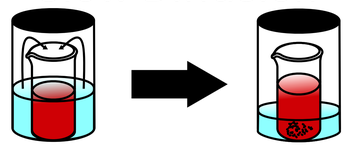
Slow Evaporation



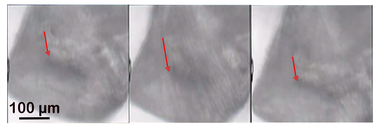
40 °C → -20 °C → 40 °C



Slow Diffusion

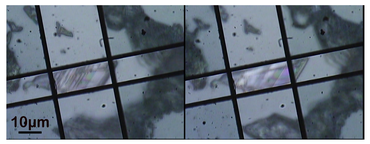


40 °C → -20 °C → 40 °C

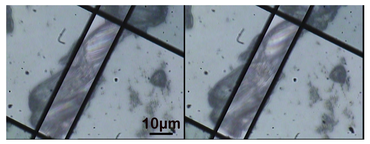


Both methods produce polycrystals when crystallization is performed at room temperature, shown by the clouded apperance. These crystals show inverted expansion behaviors.

-20 °C ⟷ 40 °C



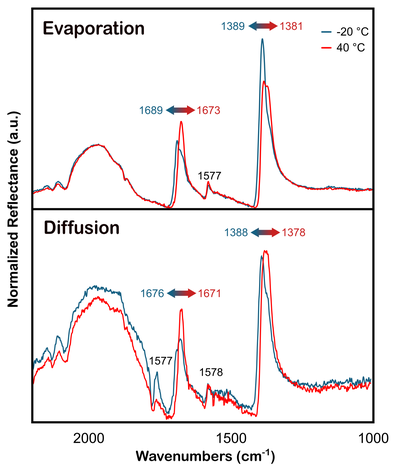
-20 °C ⟷ 40 °C



Crystallizing at 13 °C gives single crystals and polycrystals. These crystals show both reported and inverted expansion behaviors.

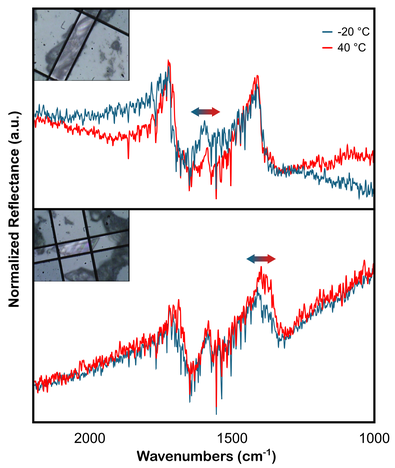
Phase-Dependent FTIR Response

Polycrystals



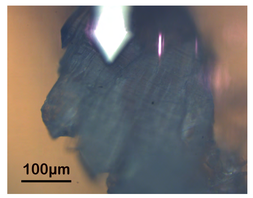
In far-field FTIR spectra, polycrystals show mild shifting of peaks between hot and cold states, likely corresponding to changes in out-of-plane hydrogen bonding interations.

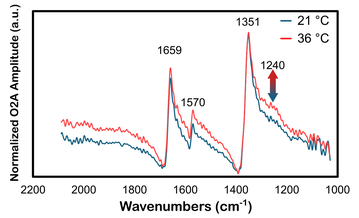
Single Crystals



Due to small sizes, signal is reduced for single crystals, and peak positions are difficult to assign properly. Mixed behaviors are seen, some peak shifts corroborate bulk shifts while others are novel.

Near-Field IR Response

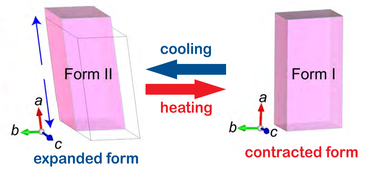




Minimal changes were observed, likely due to limitations with temperature control inside of the s-SNOM instrument.

Conclusions & Future Work

Bulk polycrystalline guanidinium nitrate shows thermosalience shown through mechanical deformation and changes in reflectance; however the change is inverted to that which is reported in previous literature.

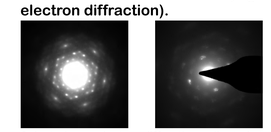


Single crystal GN show both the reported and the inverted behavior, with mixed impacts on the infrared response.

Future work aims to:
Validate behavior with larger single crystallites.

New temperature controlled "crystal growth chamber"

Verify inverted expansion using diffraction experiments (e.g. electron diffraction).



Selected area electron diffraction collected at room temperature.

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References

(1) Conley, H. J., et al. Nano Lett. 2013, 13 (8), 3626–3630. https://doi.org/10.1021/nl4014748.
(2) Folland, T. G., et. al. Nat. Commun. 2018 91 2018, 9 (1), 1–7. https://doi.org/10.1038/s41467-018-06858-y.
(3) Karothu, D. P.,et al. Nat. Commun. 2022, 13 (1), 1–10. https://doi.org/10.1038/s41467-022-30541-y..