Terahertz-Induced Crystallisation of Amorphous Systems

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***Abstract*— We performed initial experimental studies on inducing crystallisation in amorphous organic compounds with intense terahertz radiation generated by the free electron laser FLARE of the FELIX Laboratory. By performing careful experiments we minimized the role of thermal heating and show that there is a different behaviour between THz-induced and thermal-induced crystallization.**

I. INTRODUCTION

TERAHERTZ radiation excites inter-molecular vibrational (librational) responses in amorphous systems, represented in the vibrational density of states (VDOS) [1]. Upon crystallization of an amorphous sample the VDOS collapses into a limited number of phonon modes. With the advance of free-electron laser sources the generation of highly intense terahertz pulses has become possible.

The FLARE beam line at the FELIX Laboratory in Nijmegen, The Netherlands, produces a beam consisting of trains of micro pulses (length of 10-100 ps). Each train forms a macro pulse of about 10 μs length. The average power output at the diagnostic station where the experiments are performed was approximately 200 mW when the output frequency is around 1 THz, resulting in a micropulse power of ≈ 2 MW, which corresponds to a power density of 40 $MWcm^{-2}$ when focused using a *f*/6 lens. Such a terahertz beam provides enough energy to disturb the inter-molecular hydrogen-bonded network and to induce changes of state in organic molecular systems.

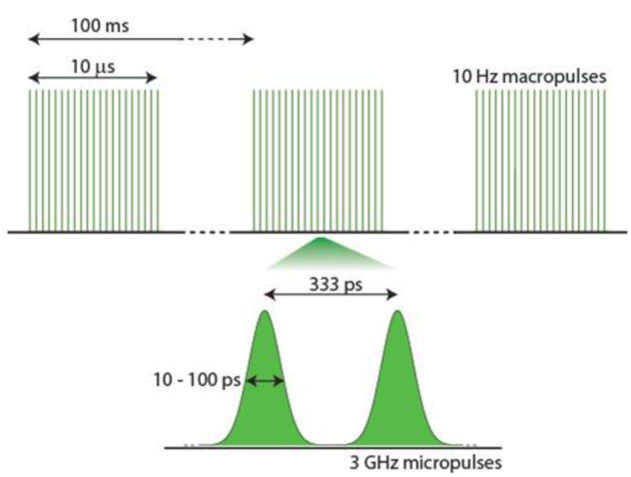

Fig. 1. The time profile of terahertz pulses produced by FLARE.

We performed first experimental studies on inducing crystallisation in amorphous systems using intense terahertz radiation. We have been able to induce the crystallization in amorphous carbamazepine (CBZ) and indomethacin (IMC). Particular care was given to exclude the role of sample heating in the crystallisation process under radiation of the FLARE beam.

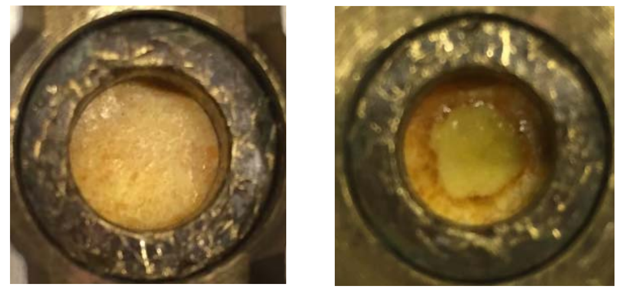

Fig. 2. (a) Freshly prepared pellet of amorphous carbamazepine, standing at room temperature. (b) Pellet after 50 minutes exposure to FLARE at room temperature. THz-TDS confirmed that sample crystallised into form I, irrespective of FLARE operating frequency at 1.0 THz (characteristic peak of form I) and 1.56 THz (characteristic peak of form III).

II. RESULTS

In the first instance, all crystalline sample materials were melted, quench-cooled using liquid nitrogen and pressed into pellets at room temperature. It was ensured that the samples were amorphous before the exposure by measuring their terahertz spectra using a THz-TDS setup. Upon exposure to the FLARE beam at room temperature for a few minutes, the areas that were exposed to THz radiation had fully crystallised (Fig. 2). Throughout all experiments we monitored the temperature of the samples using an IR thermometer. The temperature of the pellets never exceeded 330 K, which is well below the typical crystallisation temperature of the material.

In the first experiment we examined a CBZ pellet maintained at ambient conditions with no external heating or cooling and exposed the sample pellets to the FLARE beam tuned to either 1.00 THz or 1.56 THz, reflecting on the spectral features of form I and III [2]. The exposure to FLARE resulted in a radiation induced heating of the samples to temperature of ~ 326 K in 100 seconds and remained constant for longer exposures. The formation of a distinct spot on the sample surface was observed (Fig. 2b). Subsequent THz-TDS confirmed that the amorphous CBZ pellet converted into a crystalline form I irrespective of the FLARE frequency.

In the second experiment we examined the effect of the FLARE beam on an amorphous CBZ pellet kept under vacuum in a cryostat at 100 K for 14 minutes, which was then heated to 300 K at a rate of 30 K min^{-1} with continued exposure to FLARE. The sample eventually equilibrated at 327 K. The total exposure time to FLARE was 31 minutes. THz-TDS analysis did not confirm the presence of any crystalline polymorph at the end of the experiment.

In the third experiment we stored a sample of amorphous CBZ prepared on a silica window sample under vacuum in a cryostat and cooled the sample to 240 K. The pellet was exposed to FLARE at 1.56 THz for 800 s while the bulk sample temperature was kept at 240 K. Subsequently the exposure was stopped and the sample was heated to 326 K over a period of 37 minutes. This experiment served to investigate three questions: 1) whether FLARE can induce crystallisation at temperatures below the glass transition temperature, $T_g \sim 325$ K [2]; 2) whether a reduced transient heating effect by the micropulses of the FLARE pulse train can be observed since the heat should be more rapidly dissipated by the silica window, given the thermal conductivity of UV silica is 1.38 W m^{-1} K^{-1} while that of air is 0.024 W m^{-1} K^{-1}; 3) whether the effects of FLARE on nucleation and crystal growth are separable. It was found that a visually observable crystalline seed was produced in the region exposed to FLARE after 1000 s (i.e. 200 s into reheating the sample) when the recorded temperature of the region was 280 K. Localised crystal growth is observed in this region over the next 60 s and then no further growth is seen (Fig. 3b). At 40 minutes and a sample temperature of 326 K, crystal growth begins to occur from the sides of the sample, eventually resulting in the crystallisation of the entire sample (Fig. 3c). The fully crystalline sample exhibits two visually distinct regions, suggesting the possibility that both polymorphs had crystallised during the experiment. Terahertz spectra of the two regions support the fact that form III crystallised from the sides at temperatures above T_g, forming the bulk of the crystalline material, while form I crystallised at the region that was exposed to FLARE.

The experiments with amorphous CBZ indicate that intense terahertz radiation can trigger crystallisation of amorphous solids to a different polymorph than the one expected due to pure heating effects. In all cases investigated, exposures of CBZ to intense THz radiation causes crystallisation into form I, while the pure heating effect would result in form III. The form I is obtained even when the frequency of the incident FLARE beam is varied between 1.0 and 1.56 THz. This suggests that it is not possible to direct crystallisation into specific polymorphs for CBZ using intense terahertz radiation at a single frequency.

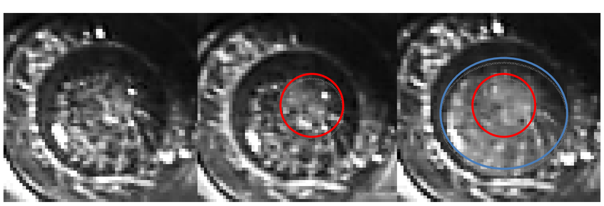

Fig. 3. (a) Amorphous CBZ at 240 K, (b) CBZ sample at 280 K after initial 1000 s of exposure to FLARE with crystallised region highlighted in red, (c) CBZ sample after heating to 336 K, crystalline region at FLARE spot highlighted in red and bulk crystalline region highlighted in blue.

Similar to CBZ, we prepared pellets of IMC (indomethacin) stored at ambient conditions with no external heating or cooling and exposed them to the FLARE beam at either 1.00 THz or 1.56 THz. In both cases the sample temperature rises fast and reaches thermal equilibrium at around 330 K (T_g = 315 K) after approximately 120 s. In contrast to the CBZ system, a distinctive glassy region rapidly forms in the area where the beam is focused. With prolonged exposure to FLARE over 2.5 minutes, crystalline centres appear within the glassy region. As with CBZ, it was demonstrated that the glassy region always forms only at the FLARE beam spot by rotating the samples. Without the exposure by FLARE, the crystallisation of IMC at these temperatures occurs over a period of several days [3].

In all cases, a mixture of α and γ polymorphs has been found, supporting the result that intense terahertz radiation of a single frequency cannot direct crystallisation into a specific polymorph from the amorphous state. However, when the crystalline and glassy regions of the same sample were analysed, the crystalline region showed a higher proportion of the γ polymorph than the glassy region. For amorphous IMC, the preferred polymorph, which it crystallises into, is highly dependent on the temperature at which it is kept. When amorphous IMC is kept at temperatures around T_g, it preferentially crystallises into the γ form; while there is increasing preference for crystallisation into the α form when it is kept at increasing temperatures above T_g [4]. Therefore, pure thermal effects would cause the region at the focal spot of FLARE to contain higher proportions of the α polymorph, while the opposite is seen experimentally. These results again provide evidence that terahertz induced crystallisation does not proceed solely due to a thermal effect.

III. Summary

In summary, several important observations were made:

- Intensive terahertz radiation can induce crystallisation beyond simple heating of amorphous samples.
- The FLARE excitation frequency had no effect on the obtained polymorph.
- Intense THz radiation cannot induce (detectable) crystallisation in samples kept at very low temperature (~100 K).
- Higher intensity THz radiation of the FLARE beam leads to a faster crystallisation process.
- In general, FLARE excitation induced formation of polymorphs of the highest thermodynamic stability.

References

[1] S. N. Taraskin, S. I. Simdyankin, S. R. Elliott, J. R. Neilson and T. Lo, "Universal Features of Terahertz Absorption in Disordered Materials," *Physical Review Letters*, *97* (5), 055504, 2006.

[2] J. A. Zeitler, D. A. Newnham, P. F. Taday, C. J. Strachan, M. Pepper, K. C. Gordon and T. Rades, "Temperature dependent terahertz pulsed spectroscopy of carbamazepine," *Thermochimica Acta*, *436*, 71–77, 2005.

[3] M. Yoshioka, B. C. Hancock and G. Zografi, "Crystallization of indomethacin from the amorphous state below and above its glass transition temperature," *Journal of Pharmaceutical Sciences*, **83**, 170, 1994.

[4] V. Andronis and G. Zografi, "Crystal nucleation and growth of indomethacin polymorphs from the amorphous state," *Journal of Non-crystalline Solids*, **271**, 236-248, 2000.