3D printing of photocurable scintillating and low-background materials

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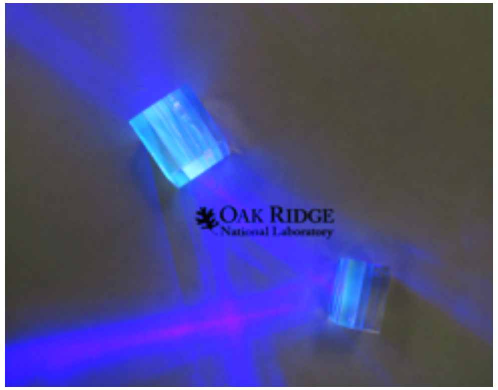
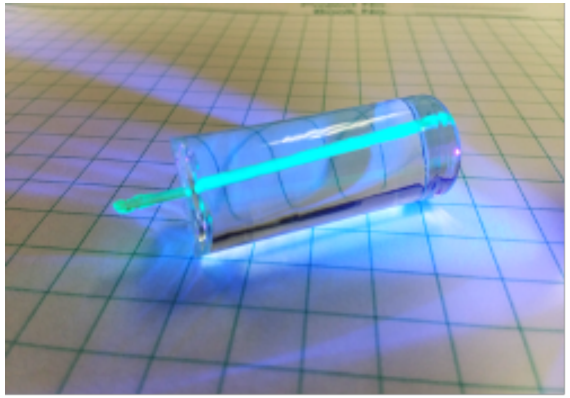
Making scintillators with *light*

- Photocurable resins allows for preparation of scintillators using just UV or visible light
  - Curing time from seconds to hours compared to multiple days for conventional approaches
  - Can be performed at room temperature
  - Resin formulations allows for embedding
- Photocurable resins are a key ingredient towards light-based 3D printing



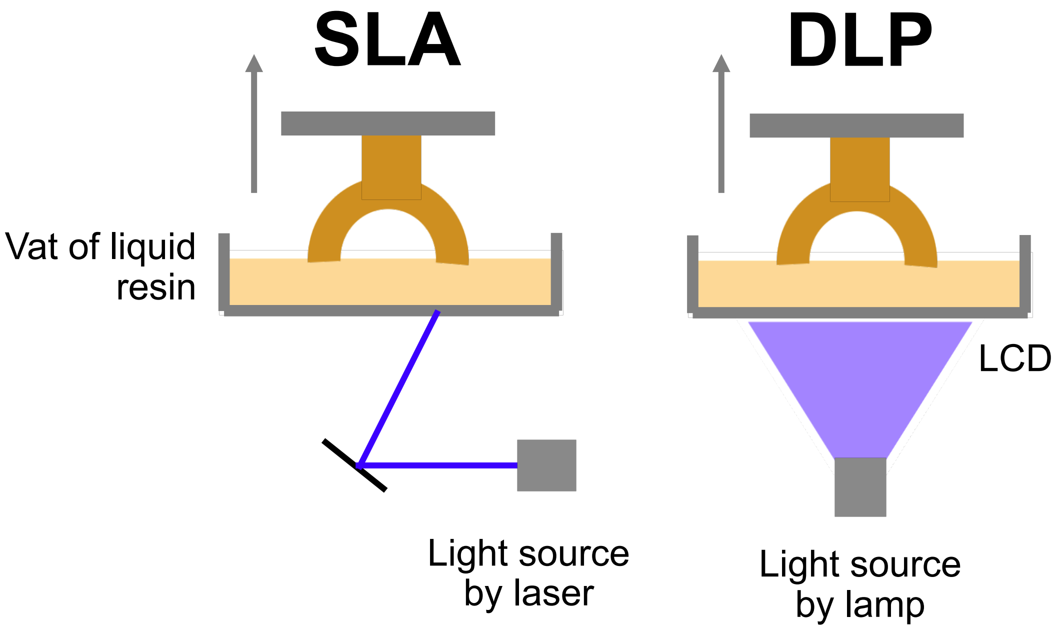


Examples of embeds – ESR reflectors (left) and WLS fiber (right)

450 nm curing station. Sample is rotated 1.2 rpm during curing

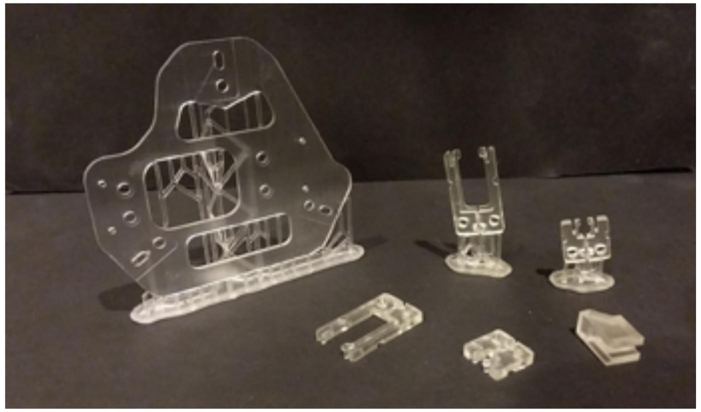
3D printing with *light*

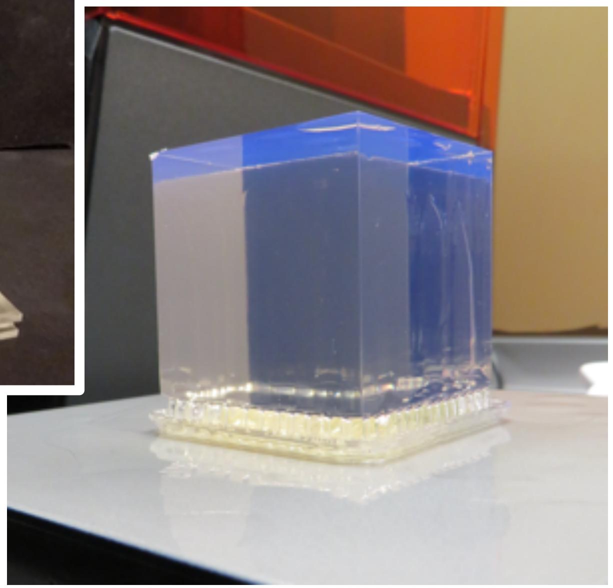
- Light-based 3D printing techniques
  - Stereolithography (SLA)
  - Digital Light Processing (DLP)
- Part is produced layer-by-layer from a liquid resin vat using just ***light***
  - Near ***contactless*** manufacturing!
- Significantly better optical properties than FDM 3D printing



https://www.forbes.com/sites/bernardmarr/2020/07/24/what-can-3d-printing-be-used-for-here-are-10-amazing-examples/?sh=41c994c54d69

https://formlabs.com/

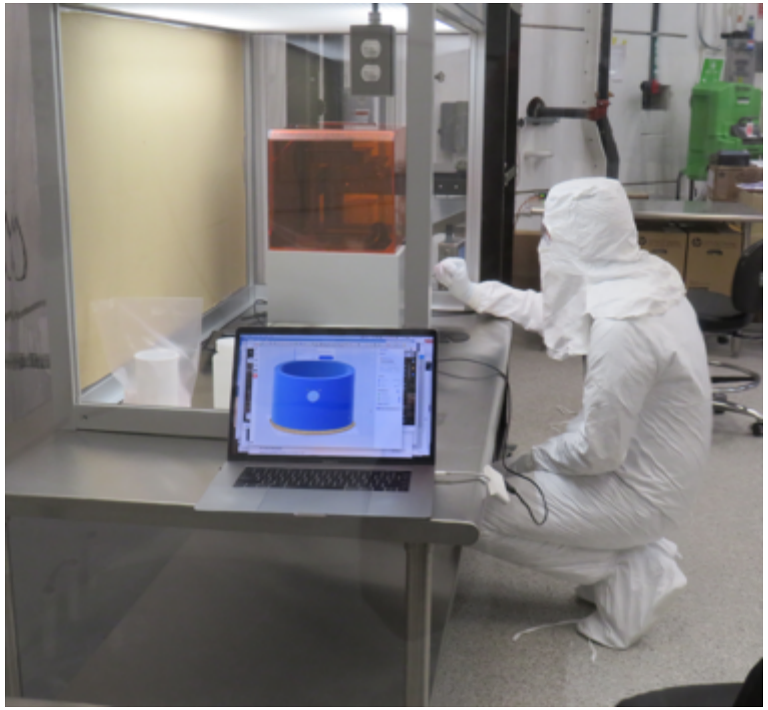


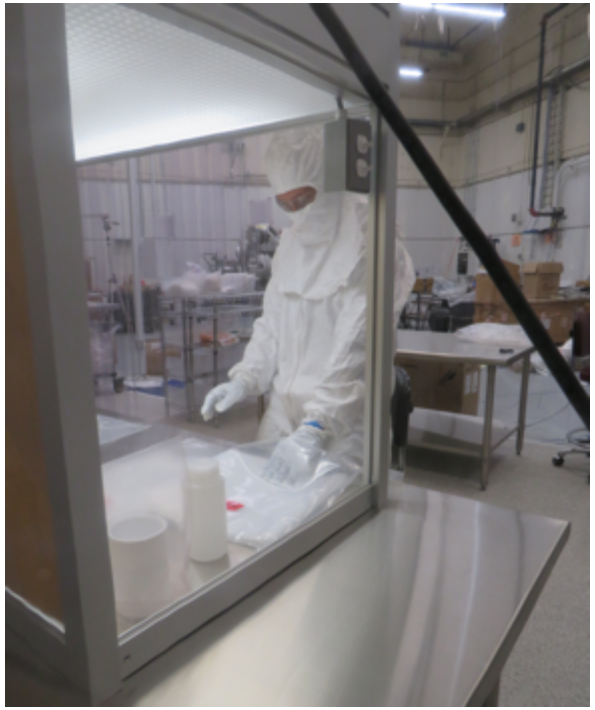


Various SLA printed components (top) and an SLA printed (2 in)^3 (right)

3D printable Low-background materials?

- SLA printing used in dental industry
  - Medical grade resins available
  - These materials are produced under strictly controlled conditions
  - May be useful as low-background materials?
- Evaluation of Formlab "*Surgical Guide*" resin as a substitute for Ultem
  - Class I Medical Device certified material
  - ISO 10993-1:2018
- ~ 800 gram solid Marinelli beaker printed for gamma assay at SURF



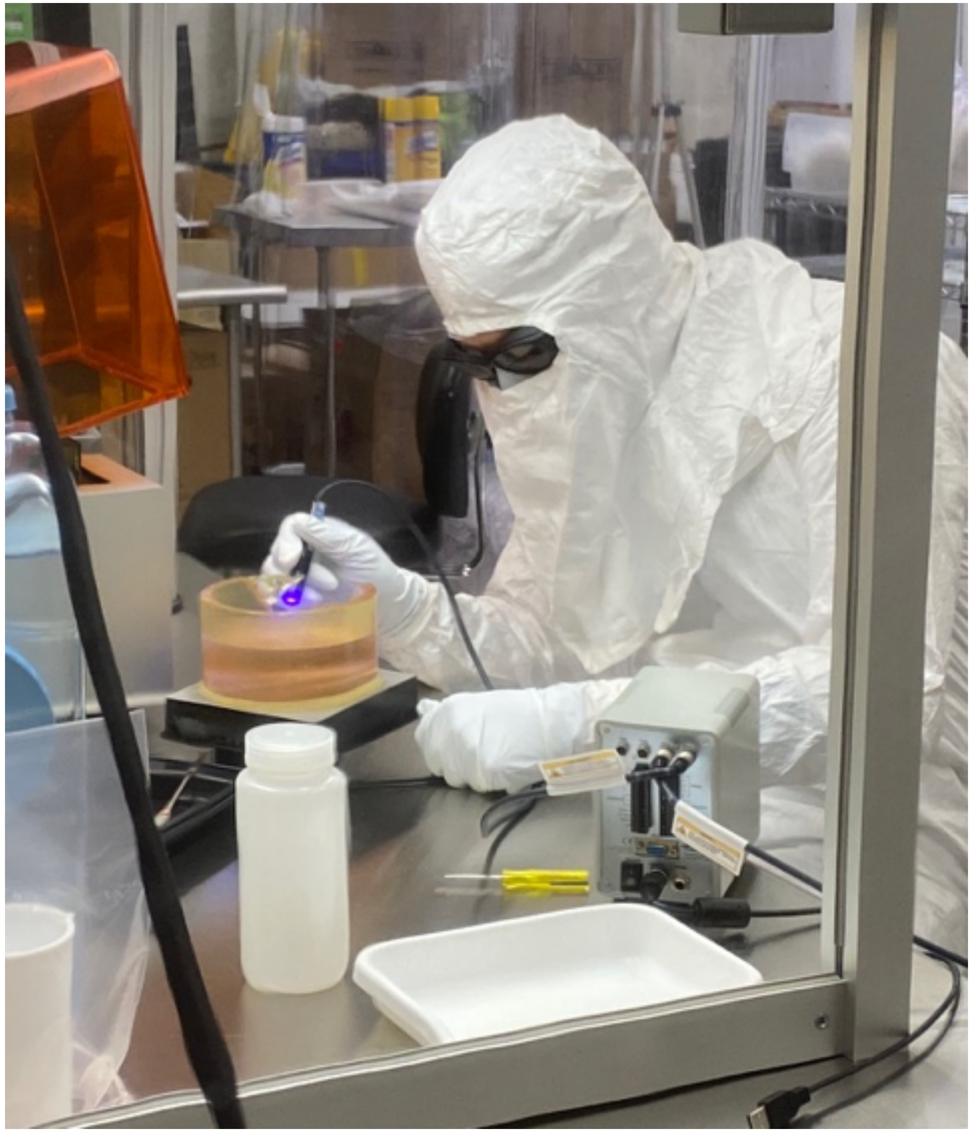


	Ultem	**Formlabs surgical resin**
Yield strength	105 MPa	73 MPa
Flexural modulus	3.3 GPa	2.9 GPa
Elongation at break	40%	12 %
Dielectric strength	327 kV/cm	258 kV/cm

Contactless joining and bonding

- 3D printing allows for production of complex parts
  - Print capsule with connectors, supports, brackets, etc
  - Geometry optimization
    - Reduce mass while retaining strength

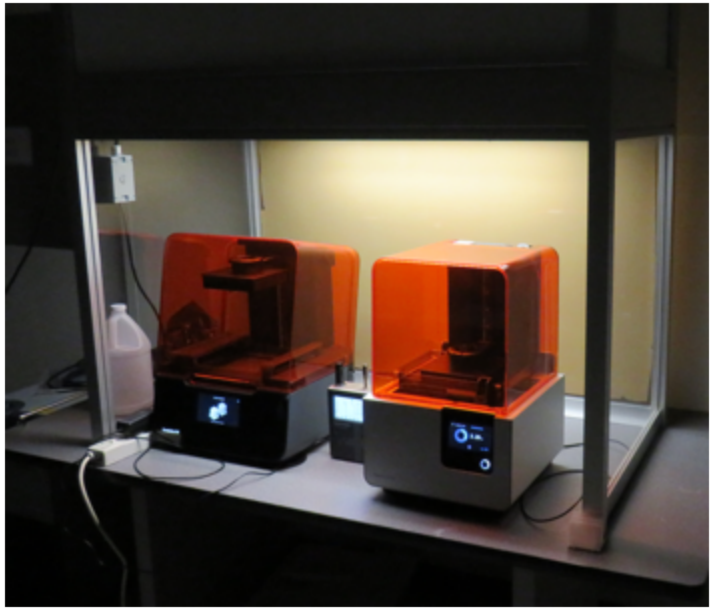
- Bonding with light
  - Photocurable resin can be cured using LED lamp
  - No direct contact with components



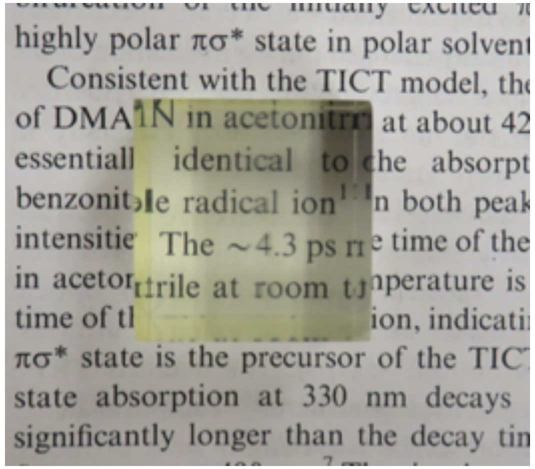
Improving 3D print quality

- Laser-based stereolithography allows for 3D printing of high transparency components
- The inherent layer-by-layer printing process can lead to optical effects
- Printing in a cleanroom or laminar flow hood helps reduce optical scattering from reduction in dust

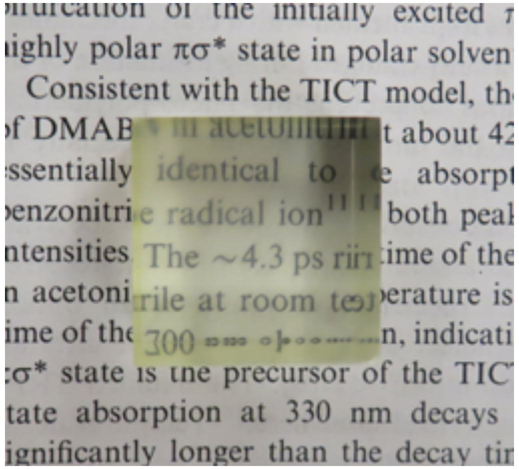
Form2 & Form3 SLA printers operating in a laminar flow hood at ORNL



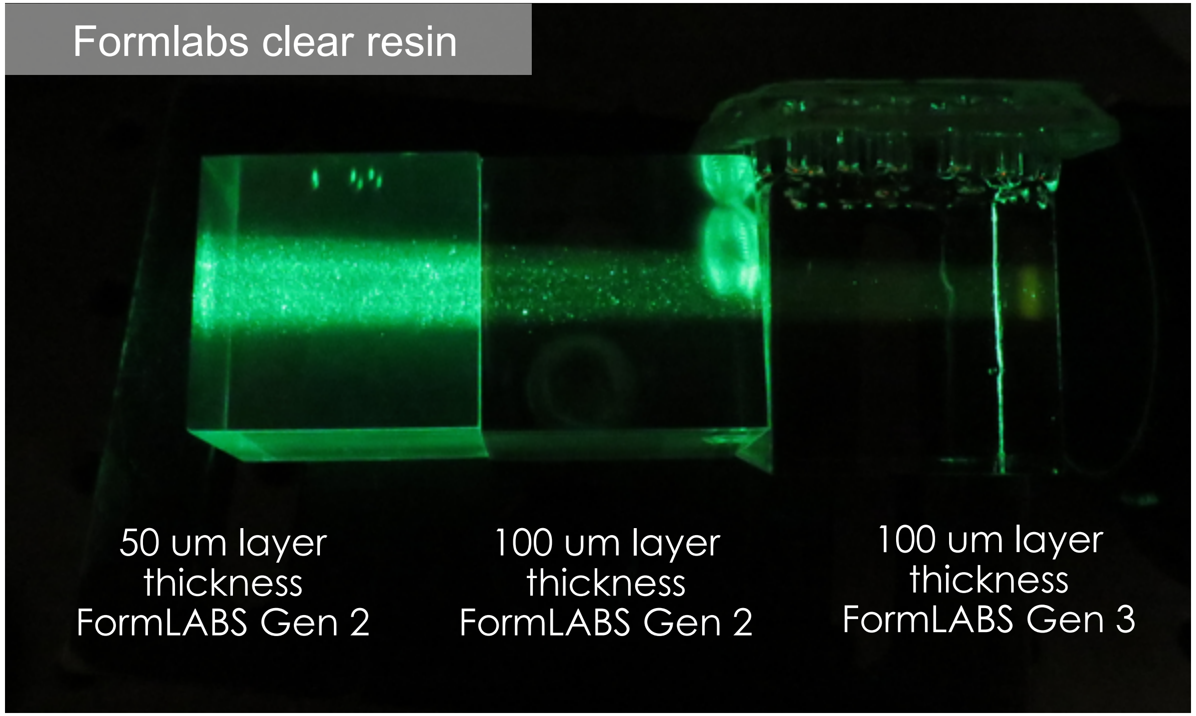
100 μm layer thickness



100 μm layer thickness *along plane*



100 μm layer thickness *against plane*

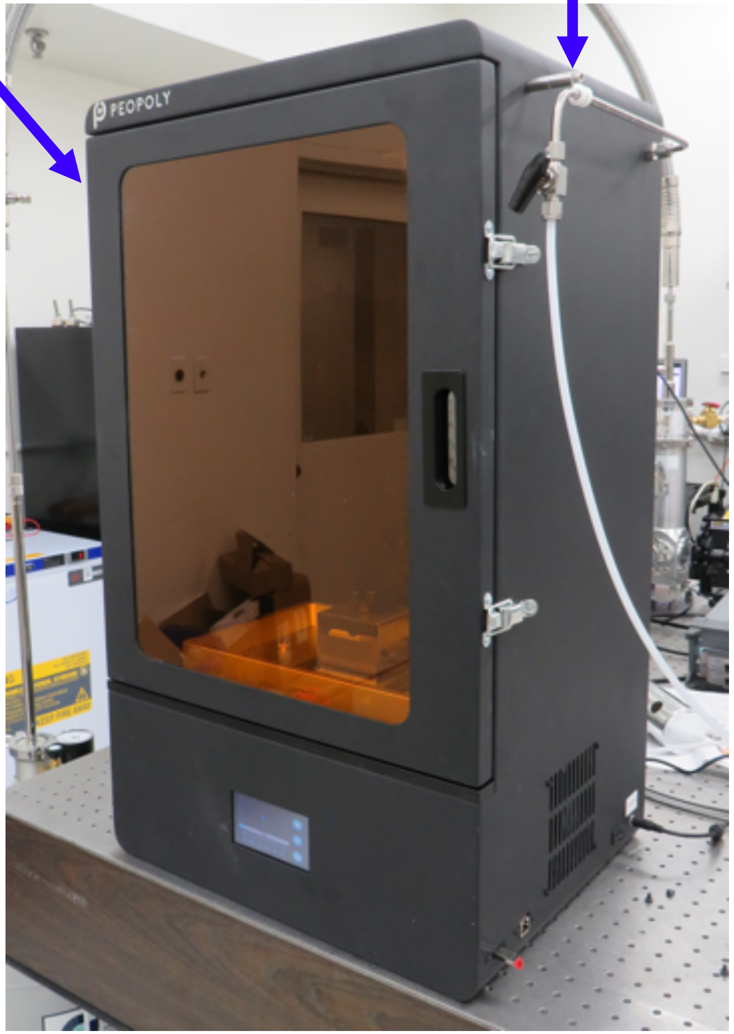


Modified DLP 3D printer

- Many commercial SLA printers use proprietary resin vats and restrict user control of settings
  - Difficult to use experimental resins
  - "*open mode*" options can be extremely expensive
- Many alternative options on the market using DLP printers
  - Easily modifiable for experimental resins

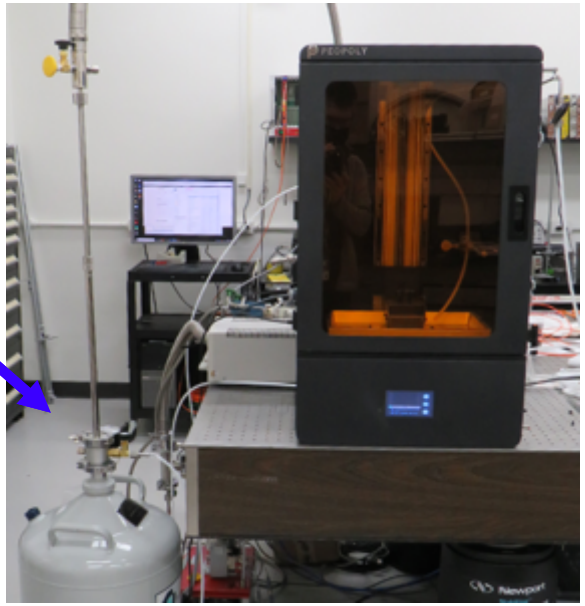
Nitrogen gas inlet

Sealed print chamber



LN_2 dewar for nitrogen boil off gas

Aluminum resin tank with FEP window

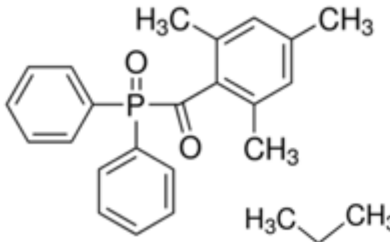


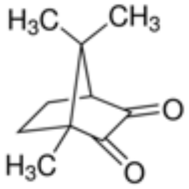
Perfect for experimental resins!

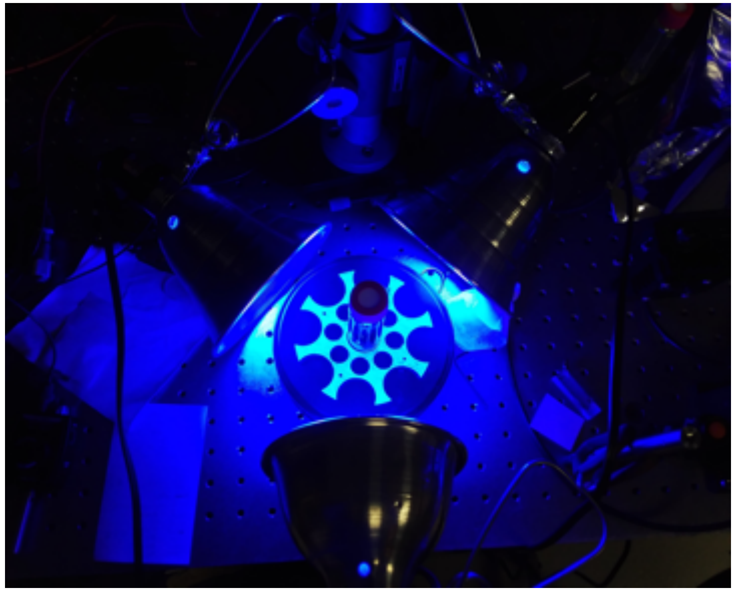
Peopoly Phenom
DLP 3D Printer

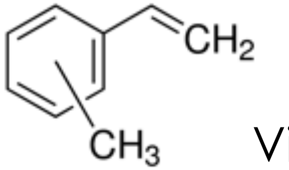
Progress towards 3D printed scintillators

- Photoinitiated free radical polymerization
- Photo initiators
  - TPO – 405 nm cure
    - Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide
  - Camphorquinone - 470 nm
- Monomer reactivity an issue for 3D printing resins
  - Nearly all commercial scintillators are made with poly(styrene) (PS) or poly(vinyltoluene) (PVT)
  - We've found the low reactivity of styrene / vinyltoluene, in a photointitated system, makes them challenging for use with 3D printing
  - Higher reactivity methacrylates or acrylates are preferred

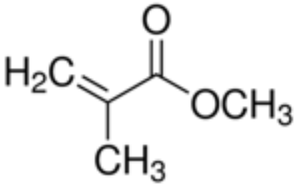




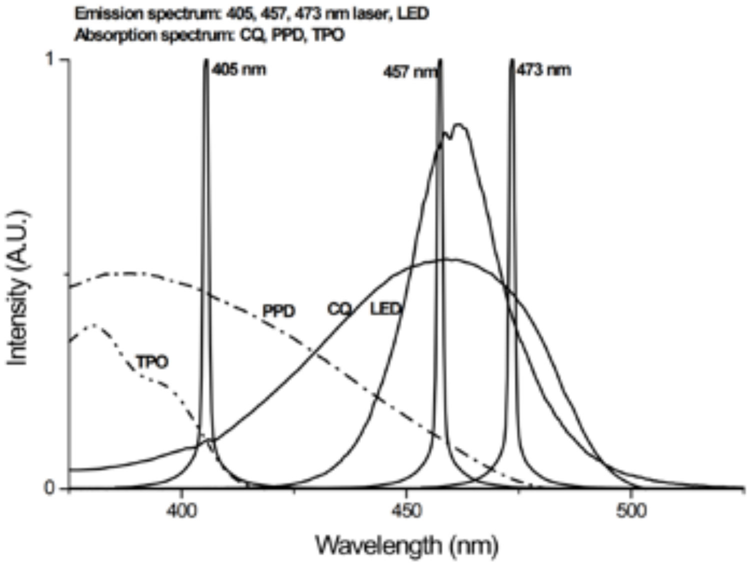




Vinyl toluene



Methyl Methacrylate



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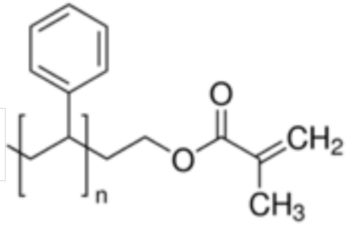
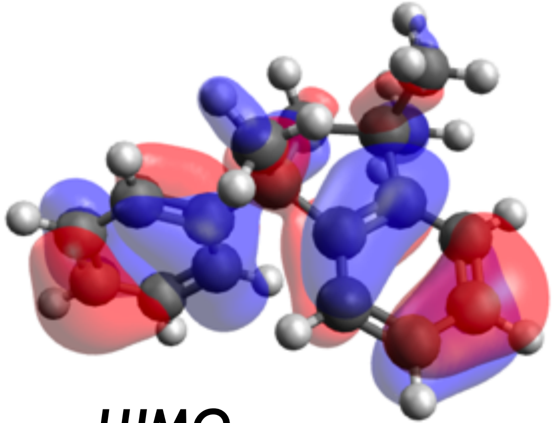
Finding an alternative to PS/PVT

- TD-DFT calculations aid in determining energy transfer efficiencies
  - Donor : Accepter spectral overlap
- Two approaches
  - Heavily doped *"PMMA-like"* matrix
    - Triethylene glycol dimethacrylate (TEGDMA)
    - Non-flammable Alkali methacrylates
    - Aromatic sources
      - 1,3,3-trimethyl-1-phenylindan (TMPI)
  - Macromonomer
    - Methacrylate terminated polystyrene

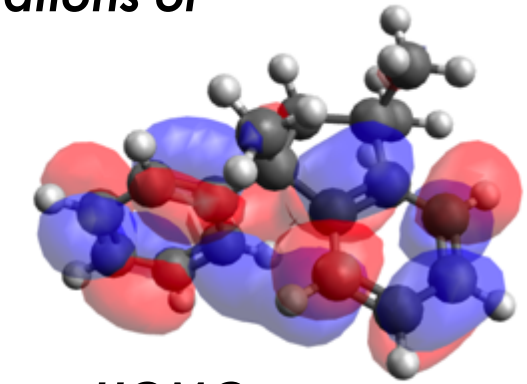


- Formulations require balance between multiple parameters
  - Printability, light yield, stability flammability, toxicity
  - Mechanical and adhesion properties

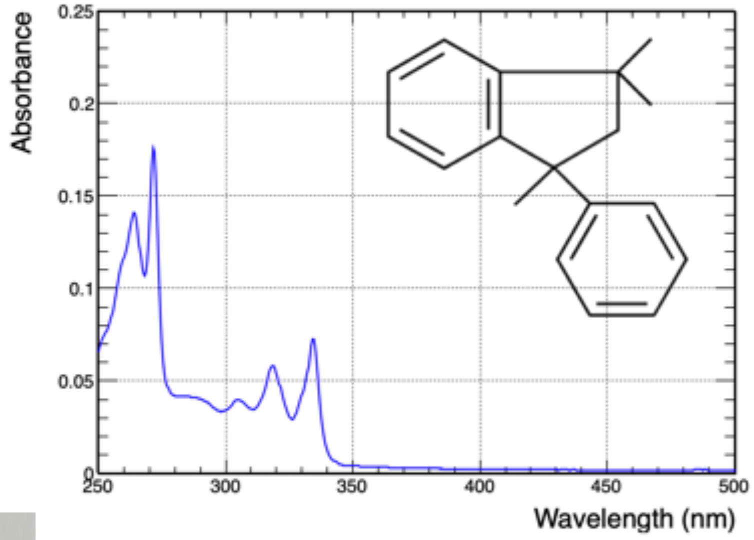
ORCA tdDFT calculations of TMPI



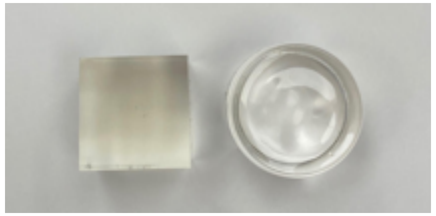
LUMO



HOMO

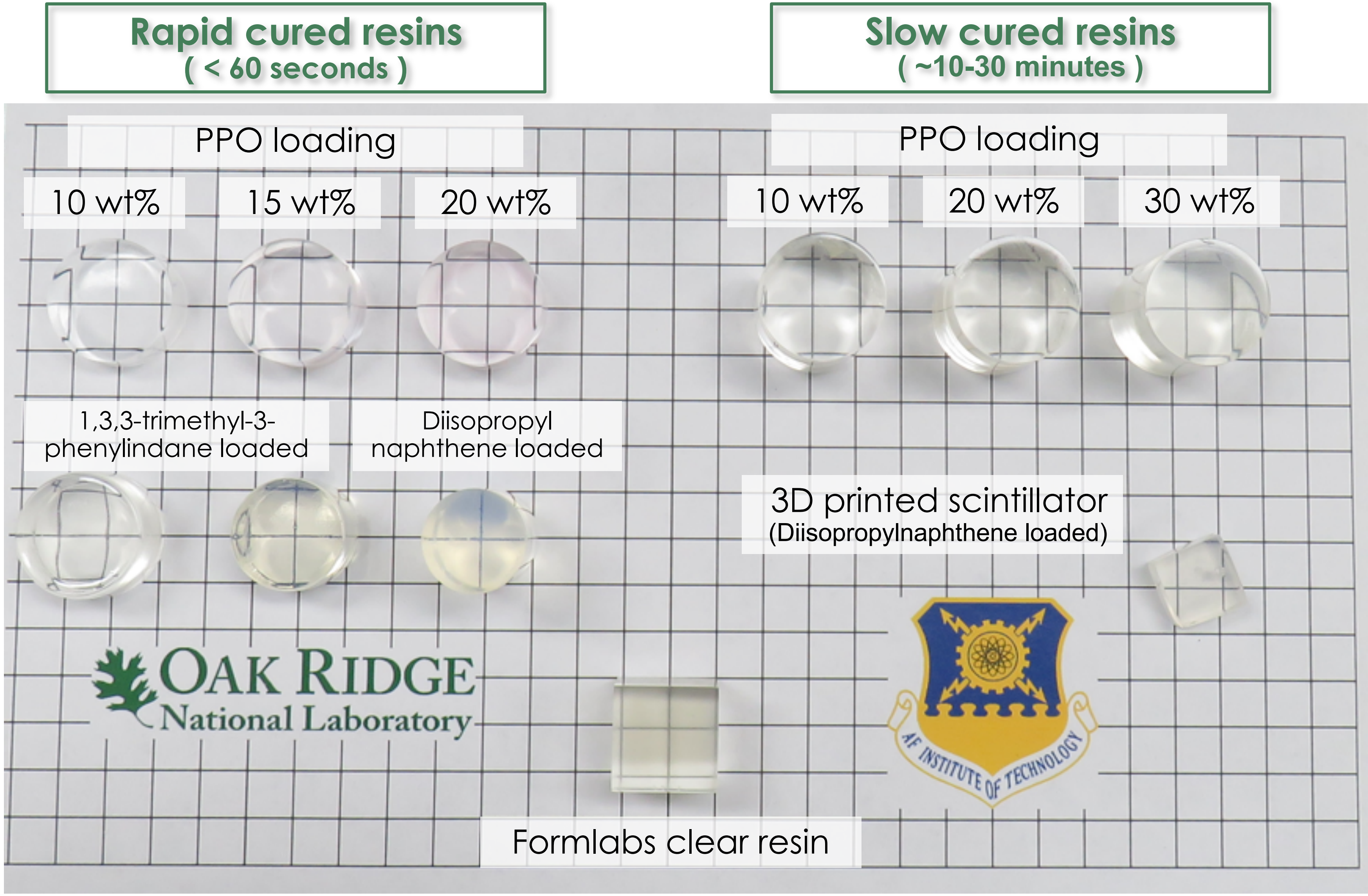


Formlabs clear **ORNL TEGDMA**



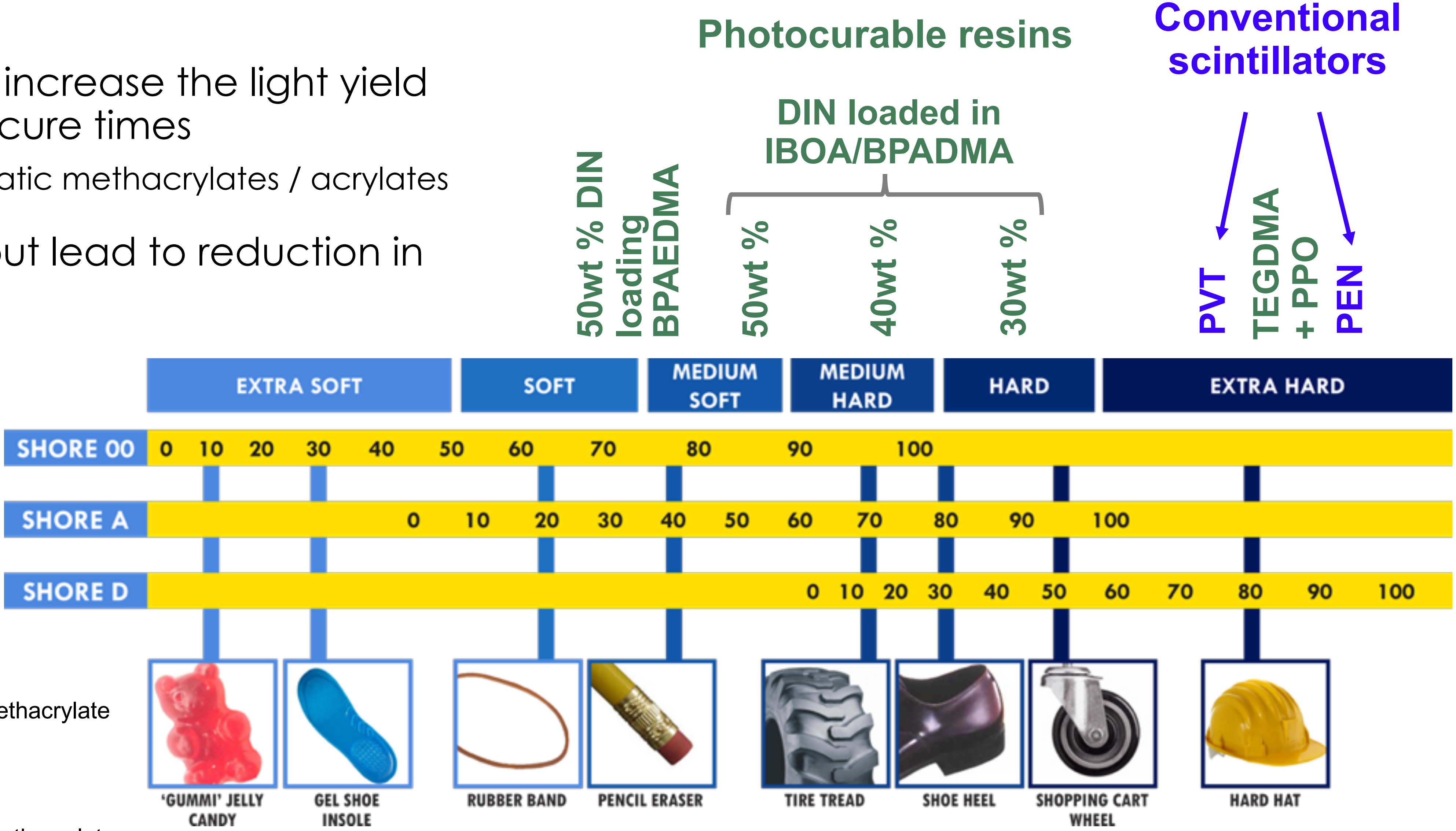
R&D on Scintillator Resin

- Slow cure resins good for photocasting of material
  - Light yield ~8000 photons / MeV
- Rapid cure needed for 3D printing applications
  - Light yield ~2000-6000 photons / MeV
  - Limited by need for methacrylate / acrylate monomers which often don't contain aromatic groups



Scintillator hardness

- Challenge is to increase the light yield while retaining cure times
  - Need for aromatic methacrylates / acrylates
- Doping works but lead to reduction in hardness



DIN – Diisopropylnapthtalene
TEGDMA – triethylene glycol dimethacrylate
PVT – Poly(vinyl toluene)
PEN – Poly(ethylene napthtalate)
IBOA - Isobornyl acrylate
BPADMA – BPA dimethacrylate
BPAEDMA – BPE ethoxylate dimethacrylate

https://www.smooth-on.com/page/durometer-shore-hardness-scale/

Conclusion

- Photocurable resins offer exciting opportunities for new instrumentation
  - Low-background materials and/or scintillators
- Opens the possibility for light-based 3D printing
  - Significant improvement in optical performance compared to FDM based printing
  - Near contactless manufacturing for low background applications
- Open questions
  - Can a rapid curing alternative to poly(styrene) / poly(vinyltoluene) be found?
  - Can the hardness be improved in heavy doped systems?
  - Interactions of dye – photoinitiators – monomers still not fully understood

Questions ?

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Maj. James Bevins, Capt. Brian Frandsen
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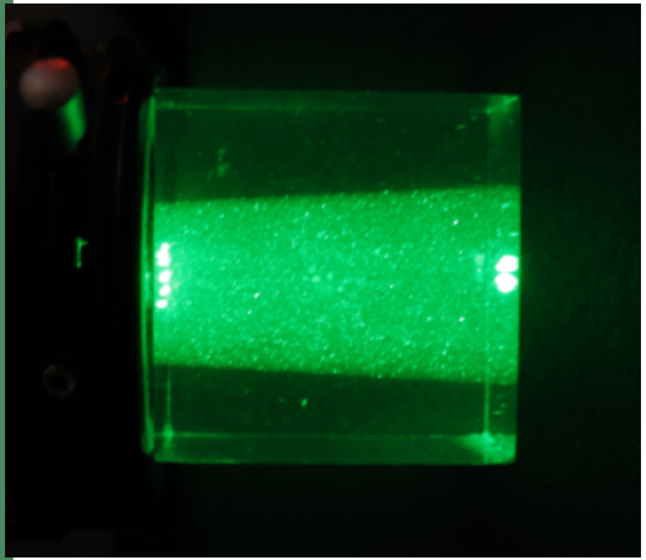
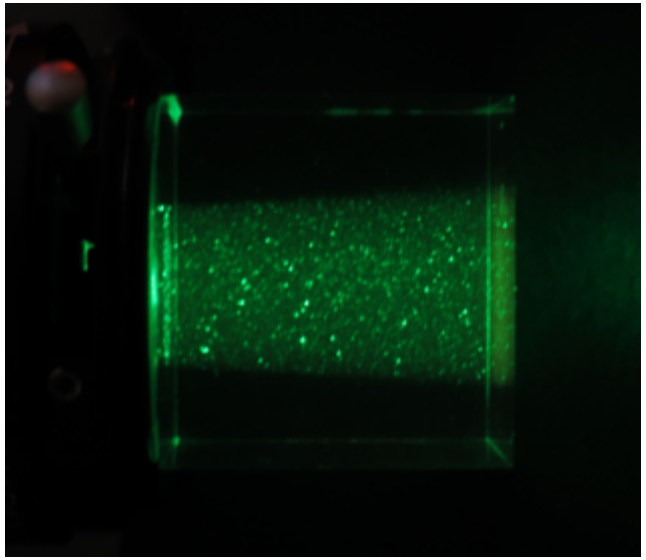
Yuri Efremenko, Brennan Hackett
University of Tennessee

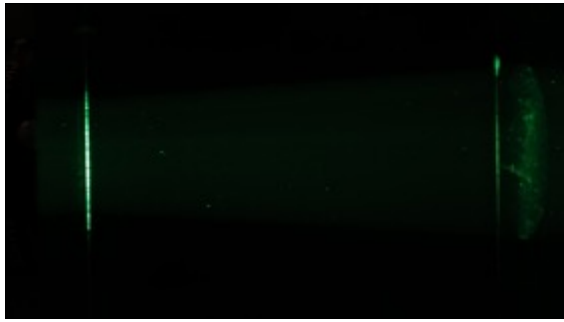


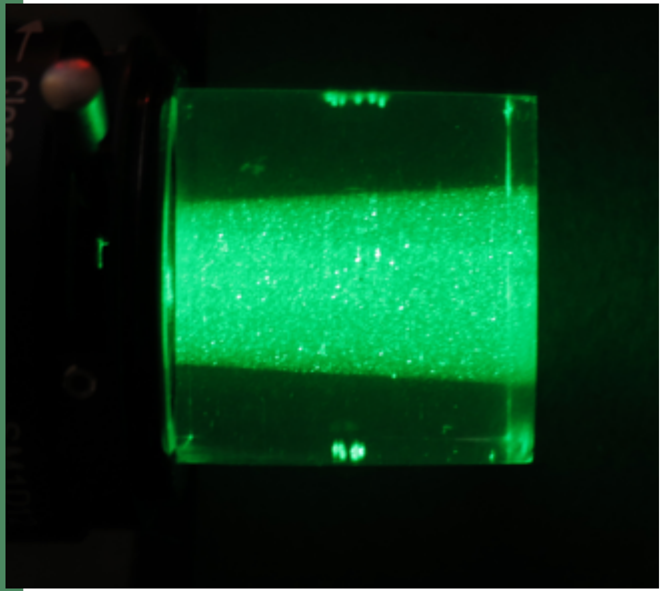
50 μm layer thickness *along plane*



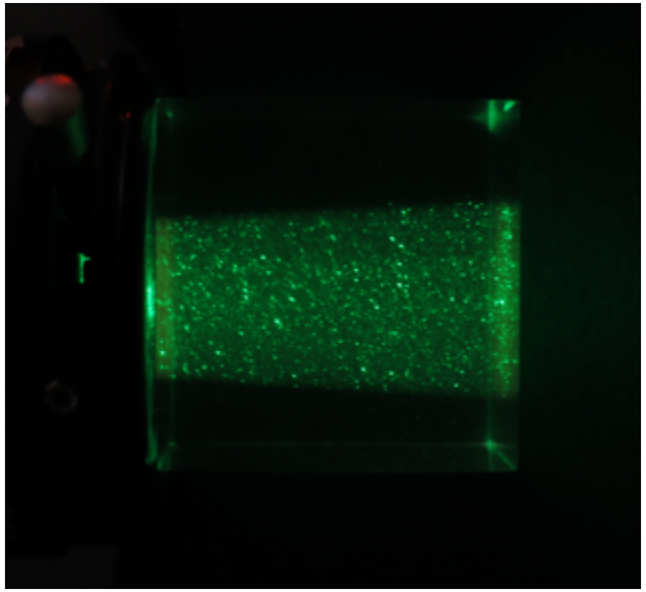
100 μm layer thickness *along plane*

EJ200 under same conditions





50 μm layer thickness *against plane*



100 μm layer thickness *against plane*

EJ200 digitally enhanced brightness