REU 2010: Investigation of $Ba_8Ga_{16}Ge_{30}$ Type I Clathrate by Pulsed Laser Ablation

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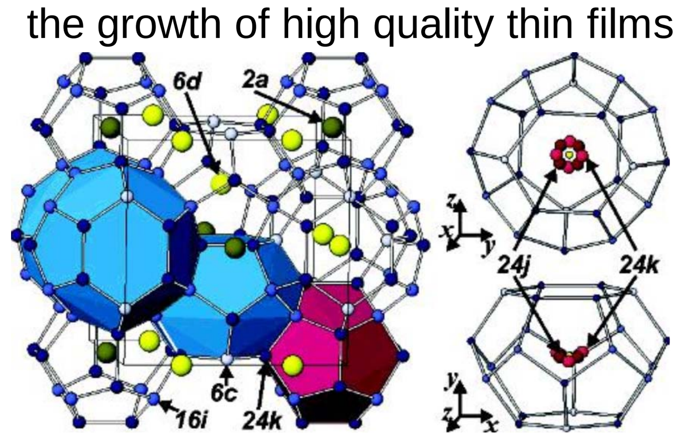
Abstract:

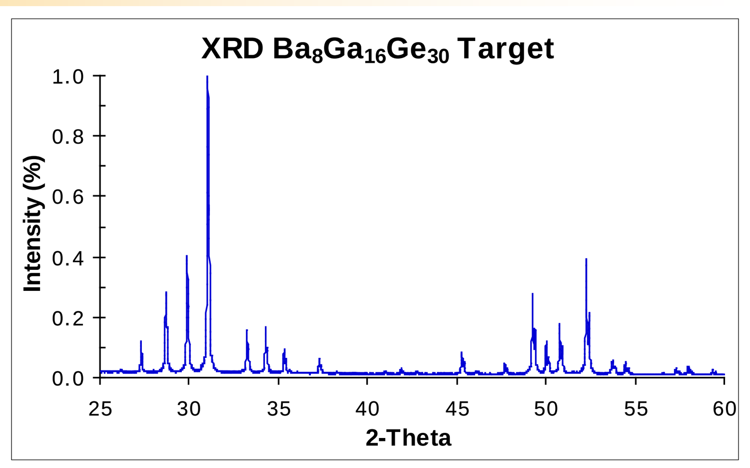
The novel thermoelectric material $Ba_8Ga_{16}Ge_{30}$ type-I clathrate was investigated through the use of pulsed laser ablation. Production of particles and droplets from ablation of low density (3.87 g/cm^3, 67% of theoretical) and high density targets (5.10 g/cm^3, 88% of theoretical) was studied. Using a scanning electron microscope, surface morphologies were examined of ablated cold- and hot-pressed targets and films deposited on (100) Si. Laser ablated plasma plumes were analyzed using ICCD imaging establishing plasma thickness. Optical emission spectroscopy identified constituent elements in ablated plumes. Film thickness at various target-substrate distances were measured to determine deposition rates for production of thick films for future work. This investigation provides a new direction towards the growth of high quality thin films for potential TE device applications.



- Ga and Ge atoms form dodecahedral and tetrakaidecahedral cages with the heavier Ba atoms trapped inside [1]
- The lattice constant for $Ba_8Ga_{16}Ge_{30}$ is 10.78 Å

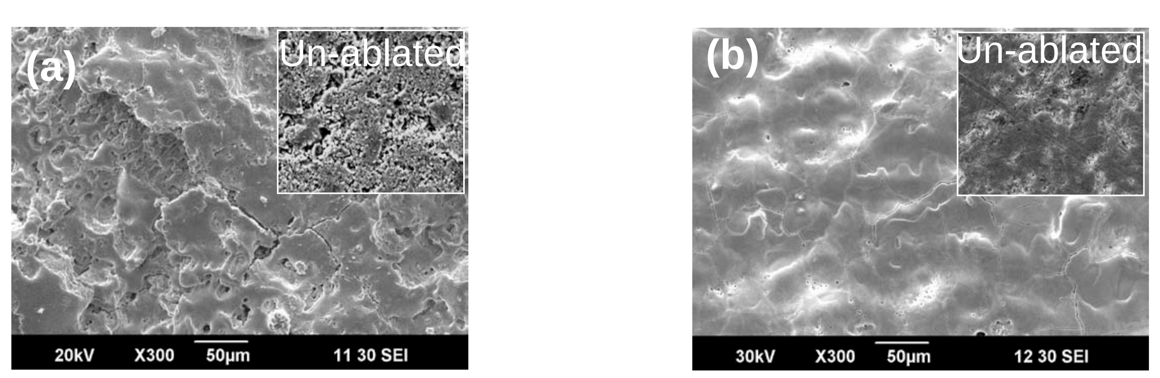
Laser-Target Interaction:

- XRD of $Ba_8Ga_{16}Ge_{30}$ target (right), structure is typical of type I clathrates



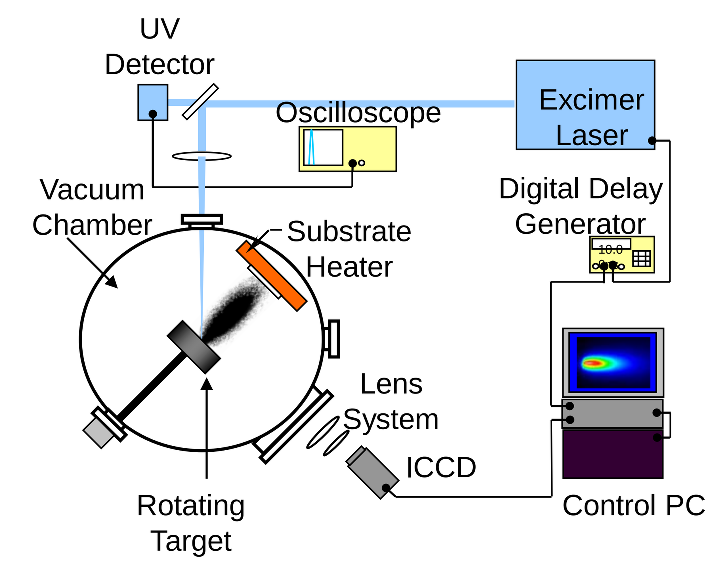
- Table 1 (below): Atomic % by EDS of $Ba_8Ga_{16}Ge_{30}$ targets. The hot-pressed target is Ga deficient and has an excess of Ge

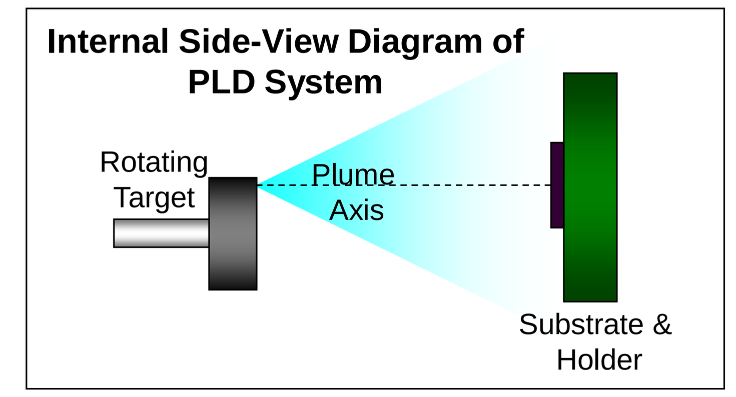
Targets	% Ba	% Ga	% Ge	Ga/Ge
Cold-Pressed	8.0 ± 0.2	18.8 ± 0.8	31.1 ± 0.6	0.6 ± 0.0
Hot-Pressed	8.0 ± 0.0	14.9 ± 0.3	34.0 ± 0.3	0.4 ± 0.0



Surface morphology of ablated $Ba_8Ga_{16}Ge_{30}$ (a) cold-pressed and (b) hot-pressed targets. Targets were ablated for 100 pulses/site at a fluence of 3 J/cm^2. A more complete melt zone is visible on the hot-pressed target.

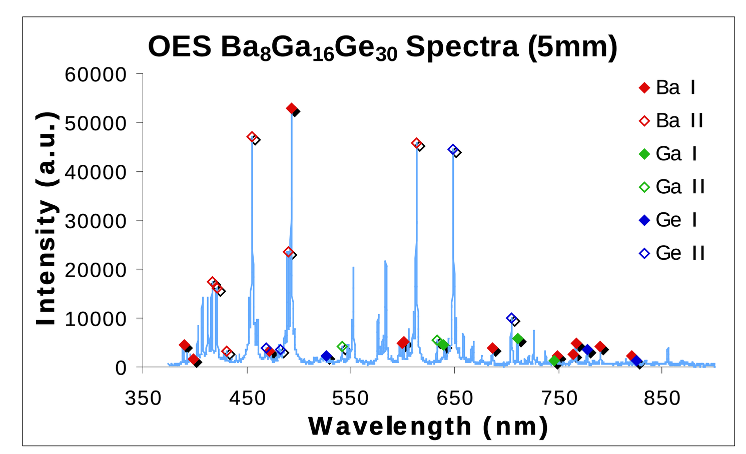
Experimental Setup:



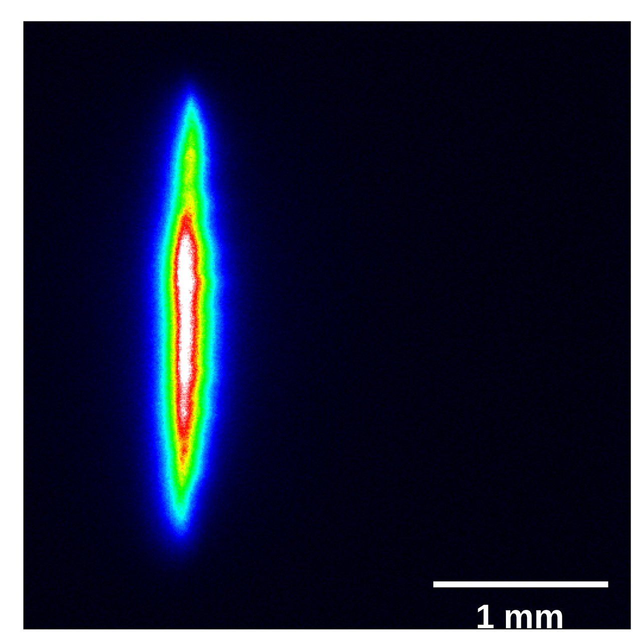


UV 248 nm wavelength KrF excimer laser, sub-microTorr vacuum system, rotating target, PI-MAX:512 digital ICCD camera system (spectrometer not shown), oscilloscope, sub-nanosecond digital delay generator

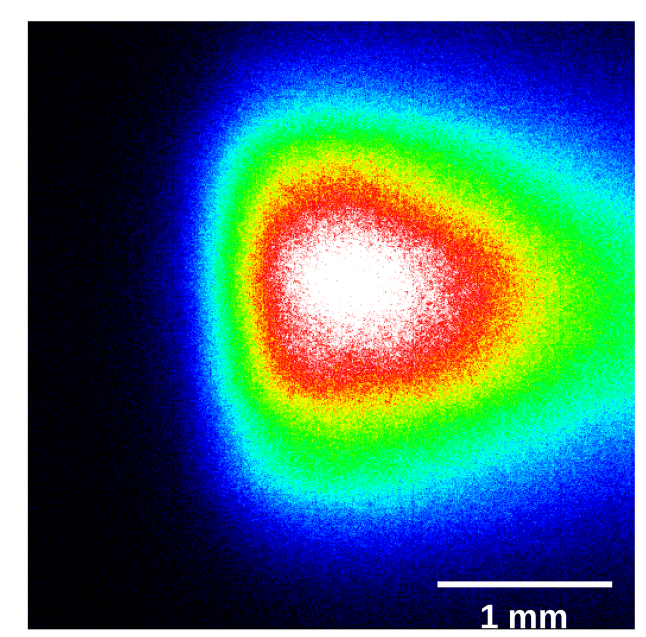
Optical Analysis:



Total emission visible spectrum of $Ba_8Ga_{16}Ge_{30}$ at 5 mm from target surface. The identified peaks represent the neutral (I) and singly (II) ionized states of barium, gallium, and germanium. High ionization and kinetic energy positively contribute to formation of quality films.



- ICCD image of 114 μm thick plasma
- 3 J/cm^2, 50 ns gate

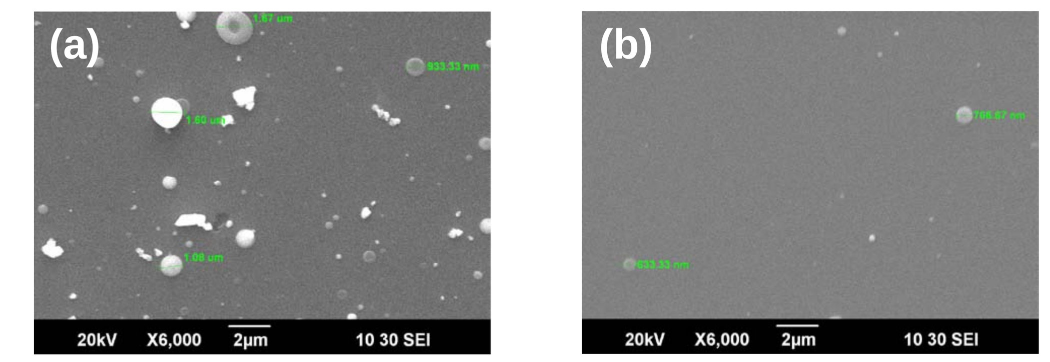


- ICCD image of evolved plume
- 3 J/cm^2, 1000 ns gate

Particle Reduction:

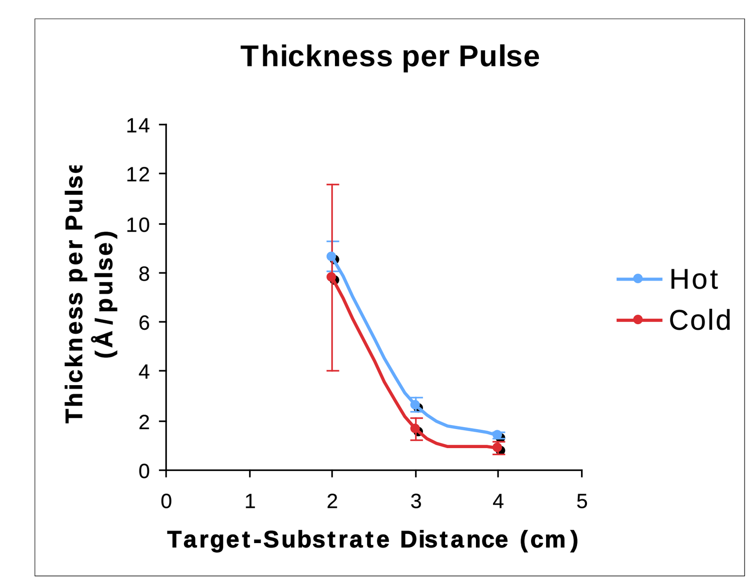
Particles (Hot)	17 ± 1
Particles (Cold)	84 ± 10

Table 2: Particle counts for 2560 Å thick films. Particles were counted at four 850 μm x 573 μm locations of each film and then averaged for particle densities.



Particle defects on films produced at 4 cm target-substrate distance by (a) cold-pressed and (b) hot-pressed targets. Films produced by cold pressed targets exhibit a far greater number, as well as, larger particle defects.

Thickness vs Target-Substrate Distance



- Cold-pressed targets have more variability in film thickness per pulse due to the high concentration of particulates
- The rapid decrease in film thickness is a result of the plume expansion
- This serves as preliminary work for future investigation of thick film (>μm 5) electric transport properties

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References:

- [1] "Crystal Stuctures of Thermoelectric n- and p-type $Ba_8Ga_{16}Ge_{30}$Studied by Single Crystal, Multitemperature Neutron Diffraction, Conventional X-ray Diffraction and Resonant Synchrotron X-ray Diffraction" Mogens Christensen et. Al, 11/17/2006, JACS Articles
- [2] "Growth and Characterization of Germanium-Based Type I Clathrate Thin Films Deposited by Pulsed Laser Ablation" Robert Hyde, 30th International Conference on Advanced Ceramics and Composites

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