The type I clathrate $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ is a promising material for thermoelectric applications due to its very low thermal conductivity resulting from high phonon scattering by the vibrating Ba atoms in the clathrate structure. We have used a dual-laser ablation process to deposit stoichiometric films of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$. In dual-laser ablation, excimer and CO$_2$ laser pulses are synchronized to enhance the initial plasma temperature to facilitate the growth of polycrystalline films with low defect densities. The crystallinity, morphology, and the stoichiometry of the films were seen to depend on the fluence of the excimer laser pulses. While low defect densities are obtained for laser fluences that are just above the ablation threshold of a $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ composite target ($\approx 0.6$ J/cm$^2$), single-laser ablation was not stoichiometric until the laser fluence reached above 1 J/cm$^2$. In contrast, under optimum growth conditions dual-laser ablation was stoichiometric for laser fluences just above the threshold. The time-of-flight and species-resolved optical emission spectroscopy investigation of plasma expansion dynamics showed that the expansion profiles of Ba, Ga, and Ge at low fluences overlapped only in dual-laser ablation, which is required for stoichiometric film growth. Results comparing the optical emission spectroscopy, morphology, and crystalline properties of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ films grown by the single and dual-laser processes are presented.

We have grown stoichiometric $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ films by the laser ablation process. Physical properties of the target favor the ejection of micron and submicron size particulates leading to poor film morphologies. All these factors positively contribute to the formation of highly crystalline films of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$. The spectral intensities were acquired in a plane 6 mm from the target. The neutral atoms from emission spectroscopy for the (a) single-laser and (b) dual-laser fluences of 2 J/cm$^2$. The dual-laser ablation results in a more complete plasma plumes at various distances from the target. Dual-laser ablated species undergo high initial acceleration and reach much higher velocities (kinetic energy).

The non-gated OES visible spectrums with the neutral (I) and singly (II) ionized elements identified for barium, gallium, and germanium. Spectrums (a) for a single-laser fluence of 1 J/cm$^2$ and for (b) the dual-laser with 1 J/cm$^2$ excimer laser fluence and the 2 J/cm$^2$ CO$_2$ laser fluence. The dual-laser spectrum shows the increased intensity of the ionized elements.

Normalized total intensity for 400 to 715 nm wavelengths, for dual-laser peak-to-peak delays with 1 J/cm$^2$/UV and 2 J/cm$^2$/IR laser fluences. (a) Spectrum intensities were acquired in a plane 6 mm from the target and at off-axes positions of 0 mm, 1.25 mm, and 2.5 mm. The minimum intensity at 100 ns peak-to-peak delay corresponds to broader plume expansion and higher energy coupling as compared to the single-laser intensity and expansion (dotted lines). (b) The total intensity cross-section where the FWHM of the single laser 1 J/cm$^2$ plume is 11.0 mm while the dual-laser plume is 19.4 mm demonstrating the broader and more energetic expansion.

Species-resolved cross-sectional expansion profiles of neutral Ba and Ga atoms from emission spectroscopy for (a) single-laser and (b) dual-laser plumes. Measurements were taken 2 cm from the target. The neutral emission lines of Ba I 577.76 nm and Ga I 417.20 nm are shown. The FWHM for the Ba and Ga lines are 8.3 nm and 8.2 nm for the single-laser, and 22.8 mm 17.3 mm for the dual-laser profiles, respectively.

Species-resolved cross-sectional expansion profiles of singly ionized Ga, and Ge atoms from emission spectroscopy for (a) single-laser and (b) dual-laser plumes. The singly ionized (ii) emission lines of Ba II 485.4 nm, Ga II 439.2 nm, and Ge II 481.5 nm are shown. The FWHM for the Ba II, Ga II, and Ge II lines are 21.4 nm, 22.0 nm, and 13 nm for the single-laser, and 18.8 mm, 15.5 mm, and 15.0 mm for the dual-laser profiles, respectively.

The non-gated OES visible spectrums with the neutral (I) and singly (II) ionized elements identified for barium, gallium, and germanium. Spectrums (a) for a single-laser fluence of 1 J/cm$^2$ and for (b) the dual-laser with 1 J/cm$^2$ excimer laser fluence and the 2 J/cm$^2$ CO$_2$ laser fluence. The dual-laser spectrum shows the increased intensity of the ionized elements.

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Species-resolved cross-sectional expansion profiles of neutral Ba and Ga atoms from emission spectroscopy for (a) single-laser and (b) dual-laser plumes. Measurements were taken 2 cm from the target. The neutral emission lines of Ba I 577.76 nm and Ga I 417.20 nm are shown. The FWHM for the Ba and Ga lines are 8.3 nm and 8.2 nm for the single-laser, and 22.8 mm 17.3 mm for the dual-laser profiles, respectively.

Species-resolved cross-sectional expansion profiles of singly ionized Ga, and Ge atoms from emission spectroscopy for (a) single-laser and (b) dual-laser plumes. The singly ionized (ii) emission lines of Ba II 485.4 nm, Ga II 439.2 nm, and Ge II 481.5 nm are shown. The FWHM for the Ba II, Ga II, and Ge II lines are 21.4 nm, 22.0 nm, and 13 nm for the single-laser, and 18.8 mm, 15.5 mm, and 15.0 mm for the dual-laser profiles, respectively.

Normalized total intensity for 400 to 715 nm wavelengths, for dual-laser peak-to-peak delays with 1 J/cm$^2$/UV and 2 J/cm$^2$/IR laser fluences. (a) Spectrum intensities were acquired in a plane 6 mm from the target and at off-axes positions of 0 mm, 1.25 mm, and 2.5 mm. The minimum intensity at 100 ns peak-to-peak delay corresponds to broader plume expansion and higher energy coupling as compared to the single-laser intensity and expansion (dotted lines). (b) The total intensity cross-section where the FWHM of the single laser 1 J/cm$^2$ plume is 11.0 mm while the dual-laser plume is 19.4 mm demonstrating the broader and more energetic expansion.

Species-resolved cross-sectional expansion profiles of neutral Ba and Ga atoms from emission spectroscopy for (a) single-laser and (b) dual-laser plumes. Measurements were taken 2 cm from the target. The neutral emission lines of Ba I 577.76 nm and Ga I 417.20 nm are shown. The FWHM for the Ba and Ga lines are 8.3 nm and 8.2 nm for the single-laser, and 22.8 mm 17.3 mm for the dual-laser profiles, respectively.

Species-resolved cross-sectional expansion profiles of singly ionized Ga, and Ge atoms from emission spectroscopy for (a) single-laser and (b) dual-laser plumes. The singly ionized (ii) emission lines of Ba II 485.4 nm, Ga II 439.2 nm, and Ge II 481.5 nm are shown. The FWHM for the Ba II, Ga II, and Ge II lines are 21.4 nm, 22.0 nm, and 13 nm for the single-laser, and 18.8 mm, 15.5 mm, and 15.0 mm for the dual-laser profiles, respectively.

Normalized total intensity for 400 to 715 nm wavelengths, for dual-laser peak-to-peak delays with 1 J/cm$^2$/UV and 2 J/cm$^2$/IR laser fluences. (a) Spectrum intensities were acquired in a plane 6 mm from the target and at off-axes positions of 0 mm, 1.25 mm, and 2.5 mm. The minimum intensity at 100 ns peak-to-peak delay corresponds to broader plume expansion and higher energy coupling as compared to the single-laser intensity and expansion (dotted lines). (b) The total intensity cross-section where the FWHM of the single laser 1 J/cm$^2$ plume is 11.0 mm while the dual-laser plume is 19.4 mm demonstrating the broader and more energetic expansion.