# Progress Report on Silica Quartz Lump	Issue date:	09/29/2024
PRODUCT NAME: Quartz Lump Silica Dioxide		

1. Product Description:	
1.1. Product:	**Expected 99.99% Pure quartz lump**
1.2. Producer:	UC Davis, HMR
1.6. Raw Materials:	**Impure Quartz Lump Silica**
1.7. Project Start date:	Aug, 2024

2. Method Specifications:	
2.1. Raw Silica Sand purity level	87.76% SiO_2
2.2. Bulk Density	1.400 g/cm^3
2.3. Particle Mean diameter:	220 µm
2.4. Expected Impurities Present:	Fe_2O_3, Al_2O_3, TiO_2, K_2O, CaO, MgO, Na_2O

1. Introduction:

The growing demand for portable power applications is pushing conventional battery chemistries to their theoretical limits. Silicon shows great potential as an anode material to boost the capacity of lithium-ion cells. However, traditional methods for producing battery-grade silicon are energy-intensive. As the global community strives for carbon neutrality by 2050, with nearly a quarter of global emissions stemming from direct industrial processes, developing zero-carbon alternatives for processes like silicon production is crucial. Femtosecond lasers in material processing, along with heat transfer challenges, have been widely studied both theoretically and experimentally. Three heat transfer regimes during laser irradiation of metals have been identified: initially, hot electrons diffuse energy, and later, thermal equilibrium is reached, with normal diffusion into the bulk. In the mid-1990s, ultrashort-pulsed lasers were found to offer key advantages: ultrahigh precision, minimal thermal damage, high material removal rates, and the ability to process almost any material. Therefore, the research project aims to develop a more energy-efficient and time-saving method for producing high-quality quartz lump silica with 99.999% purity. The project introduces a groundbreaking single-step thermal process that uses localized femtosecond laser heating to achieve extremely high purity in raw quartz lump silica. This laser-driven purification technique avoids the use of harmful chemicals, and the energy-demanding mechanical methods traditionally required for quartz lump purification.

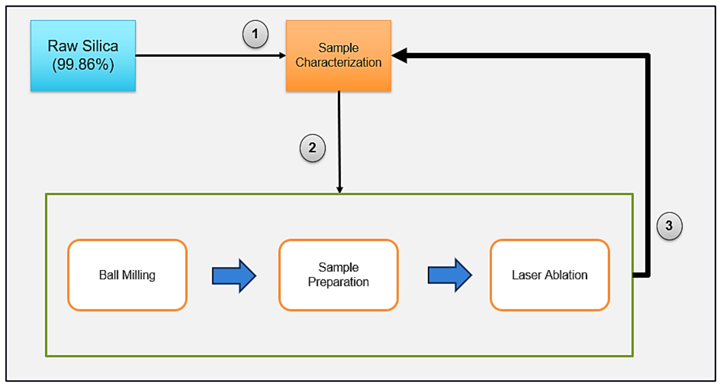
Silica, the primary raw material for silicon, is a critical component in the semiconductor and battery industries. As the demand for silicon continues to grow, driven by these industries, it is imperative to develop cost-effective methods for the purification of raw quartz lump silica.

2. Process:

This method takes advantage of delicate structural and optical effects, which are influenced by different process parameters. By carefully adjusting the laser pulse duration and intensity, the process produces unique topographical features like cones and ripples, along with favourable microstructural changes.

The laser equipment used in this process was a Tai Mai One Box Ti: Sapphire Femtosecond Laser with a power of 1.5 W and wavelength of 800nm with 80 FS laser pulse.

2.1: Ball Milling: The sample was ball milled for 15 minutes/10gm (1.5 gm/min) (With the currently available small sized lab scale ball mill). This step is required to ensure homogeneity and uniformity in the sample particles size distribution.



2.2: Sample Preparation: Post the Ball milling of the silica sand, 2 gm of the sample was sealed in Vacuum in a quartz glass test-tube using a hydrogen torch. Since, a quartz glass Transmits very well in the near infrared, including at 800 nm, with no absorption.

2.3: Laser treatment:

Img.1. Unit Process schematics.

The samples were directly irradiate :
absorb IR laser therefore the sample receives unattenuated radiation. The silica sand was exposed to laser for 2, 6, 12 and 24 h.

2.4: Procuring the Treated sample: Breaking the glass tube in a glovebox and transferring it to an airtight container for further characterization.

Laser Ablation:

- A pulsed laser irradiates a material, its energy is partially absorbed by the material. If the substrate is a metal, the transfer of energy causes the movement of the free electrons across the surface.
- The duration and environmental conditions were optimized by vacuum sealing the sample holder.

- e impurities are ablated during the process by targeting the specific wavelength for heating the impurities present in the sand. The vaporization temperature is higher for SiO2 compared to the impurities present in the raw silica sand.

  Note: All the experiments were performed at ambient temperatures and pressure.

Table.1. Table of Observations from the experiments for different time duration.

Duration Laser Treatment	Observation (if any)/Remarks
2 h (A)	Noticed Slight change in color within 5 minutes. In 1 h the discoloration becomes uniform.
6 h (B)	The sample was treated with laser for 6 hours continuously. No discoloration observed after treatment.
12 h (C)	The sample was treated with laser for 12 hours continuously. No discoloration observed after treatment.
24 h (D)	The sample was treated with laser for 24hours continuously. No discoloration observed after treatment.

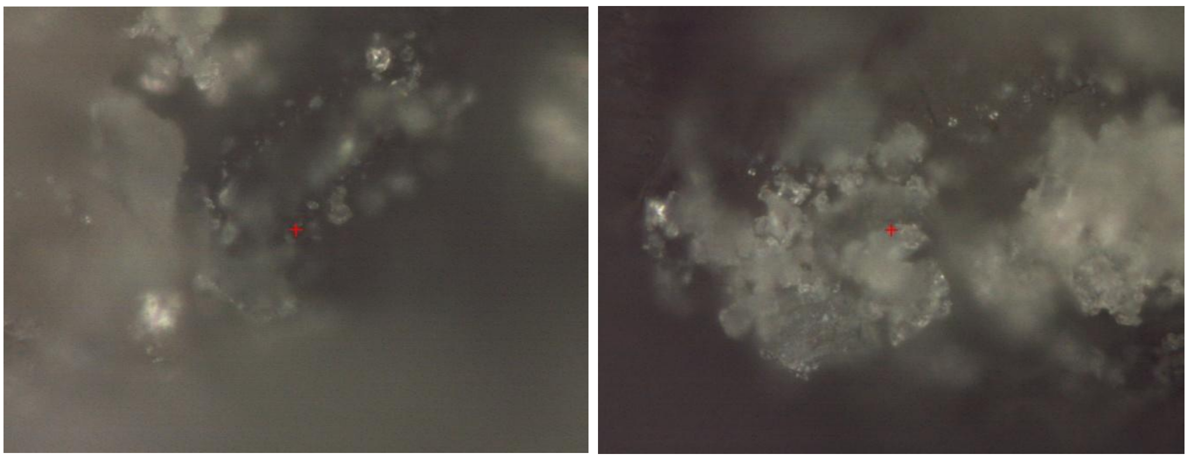
3. Characterisation and Analysis:

The following characterizations technique and analysis were conducted on both the raw quartz-lump silica sand samples as well as the laser processed silica sand.

Characterization Technique	Analysis and Conclusions
3.1. Microscopic Images:	Analysis and conclusions on Pg.4
3.2. SEM:	Analysis and conclusions on Pg.4
3.3. FTIR:	Analysis and conclusions on Pg.6
3.4. XRF	Analysis and conclusions on Pg.7
3.5. XRD:	Analysis and conclusions on Pg.8
3.6. Raman	Analysis and conclusions on Pg.9

3.1. Microscopic Images:

Microscopic analysis of the quartz lump silica sand particles was performed, this technique helps to identify the shape, colour and texture of the quartz-lump silica sand. The quartz lump silica sand was observed under the microscope at 15x resolution. The quartz lump appears like a clump of crystals. The images below is a laser treated quartz lump silica sand for 6 h at different locations.



Img. 3: Quartz lump particles under the microscope.

3.2. SEM:

Raw Quartz Lump Sand

- Mean particle size = 124.12 µm
- Max = 367.446 µm; Min: 24.6 µm

Laser Treated (6H):

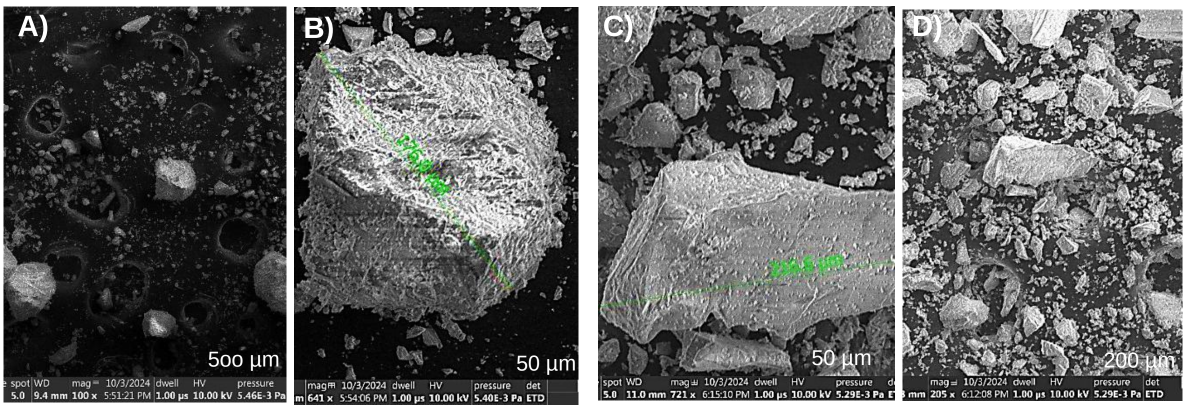
- Mean particle size = 56 µm
- Min: 24 µm; Max: 157 µm

Analysis:

The ThermoFisher Quattro S at UC Davis facility is an environmental scanning electron microscope (SEM) equipped with a Schottky field electron gun. It is capable of operating at pressures up to 50 mbar.

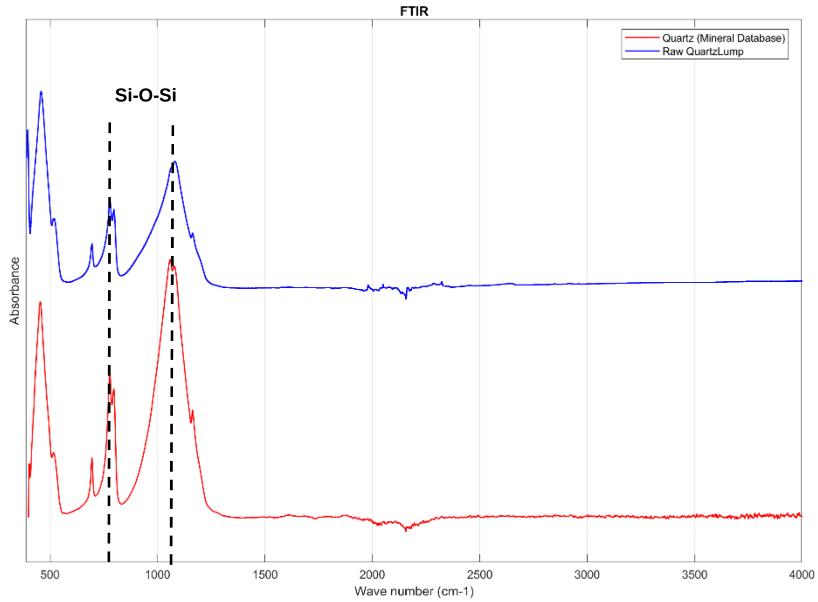
The above calculation for the mean particles size of the silica sand grains were done on Imagej software to analyse the particle size for the raw quartz-lump silica sand and the 6H laser treated silica sand. It was observed that the mean grain size of the quartz-lump silica sand was reduced from 124µm to 56 µm. This can be attributed to the effect of femtosecond laser which are known to micromachine as well as ablate the material with minimal heat damage.

The SEM images below show the comparison between the raw quartz lump silica sand and the laser treated silica sand. The scales are mentioned on each image.



Img.4: SEM images taken at different locations of the quartz lump silica sand comparing A) and B) Raw Quartz Lump silica sand; C) and D) 6H laser treated quartz lump silica sand.

3.3. FTIR:



Img.5: Comparision of FTIR for the raw quartzlump with the mineral database for quartz.

Analysis:

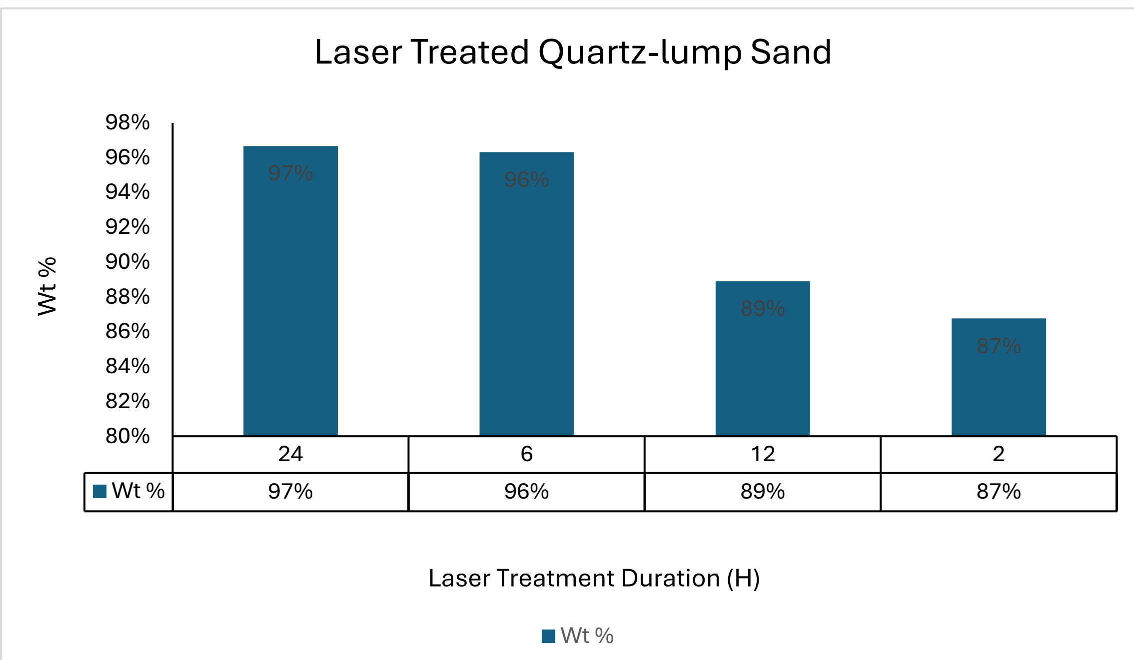
Raw quartz lump samples obtained from HMR were analyzed using an Agilent FTIR spectrometer at Lawrence Berkeley National Laboratory. The resulting spectral data were compared against reference spectra in the RRUFF Mineral Database. The characteristic FTIR absorption peaks for α-quartz, a crystalline form of silica, are typically observed around 800 cm^{-1} and 780 cm^{-1}. These bands correspond to the asymmetric stretching vibrations of Si–O–Si linkages within the quartz framework. FTIR measurements further confirm the presence of the α-quartz phase in the raw quartz lump samples.

3.4. XRF:

The X-ray Fluorescence (XRF) analysis, at the University of California-Davis was used to analyse the elemental composition of materials and compare the raw quartz lump samples with the laser treated samples at varying durations.

Equivalent weight samples were irradiated with the laser beam for 2 hour(H), 6H, 12H and 24H durations keeping the laser parameters constant. This allowed us to find the optimum duration of laser treatment for ablation of the impurities from the Quartz lump samples. The table below summarizes the percentage of SiO2 present in the samples after different laser treatment durations as well as for the raw quartz-lump silica sand.

Time (H)	Wt. %
24	96.67
6	96.31
12	88.898
2	87
Raw	87.76

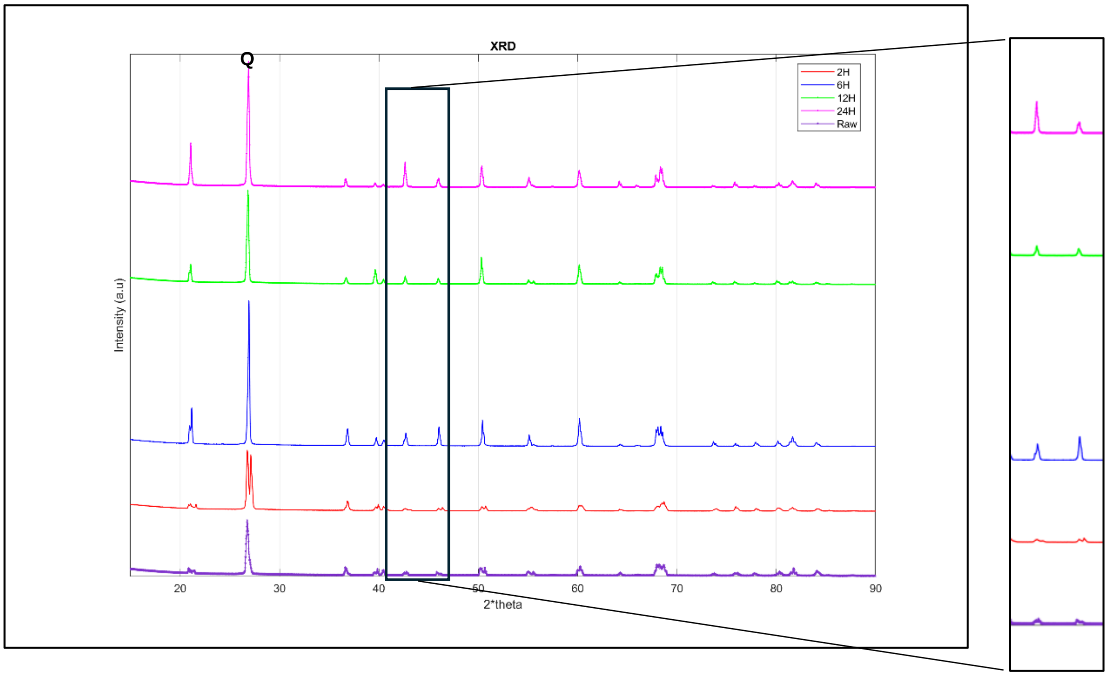


Analysis:

Based on the X-ray fluorescence (XRF) analysis, a clear correlation is observed between laser treatment duration and the SiO_2 concentration in the quartz lump samples under consistent experimental conditions. Specifically, SiO_2 content increases progressively with prolonged laser exposure, reaching a maximum of 97 wt% following 24 hours of laser treatment—an enhancement from the initial 86 wt% recorded in the untreated (raw) quartz sample. This significant improvement in purity indicates that extended laser irradiation effectively facilitates the ablation of associated impurities, thereby enhancing the overall silica content.

3.5. XRD:

X-ray diffraction (XRD) measurements were carried out using the Bruker D-8 Diffractometer at UC Davis on laser-treated powder specimens as well as the untreated quartz-lump sample to assess phase identification and degree of crystallinity



Img.4: XRD pattern of the quartz lump with different laser treatment durations

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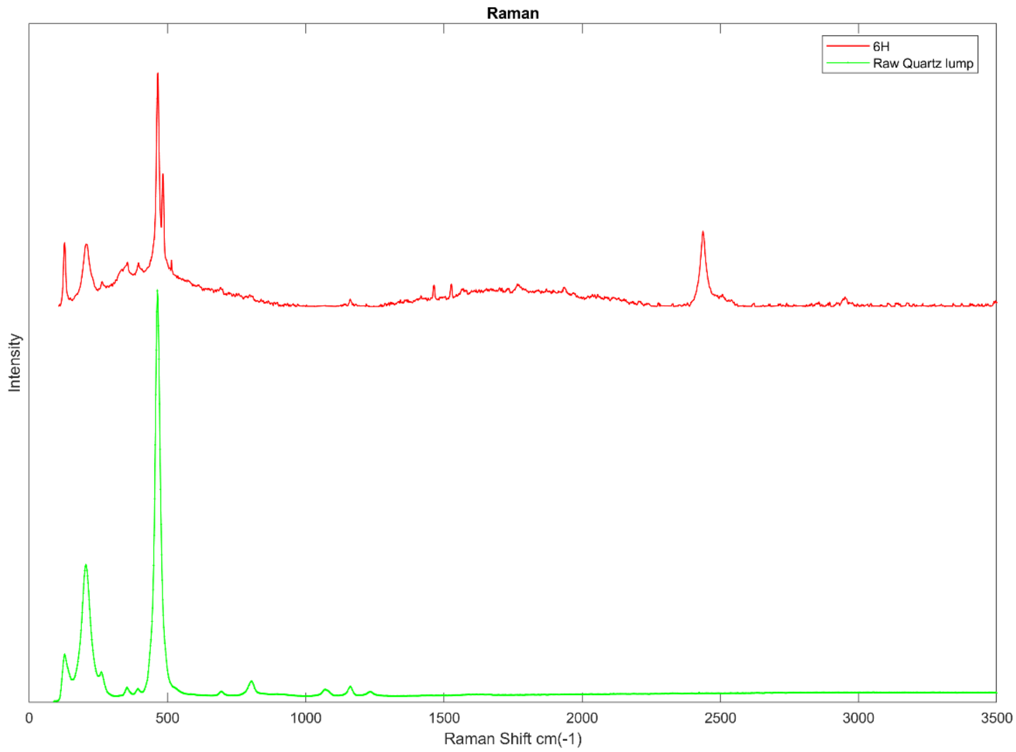
The Si–O bonding peak, denoted by “Q” for α-quartz, was observed at 2θ = 26.7°, in agreement with established diffraction standards. The diffraction peaks of the 6H laser-treated specimen was noticeably sharper and more refined when compared to the XRD profiles of the untreated quartz lump and other laser durations. These results confirm that the raw quartz lump silica sand predominantly exhibits a quartz phase. Moreover, the diffraction pattern of the untreated sample showed characteristics of a highly amorphous structure. Upon laser irradiation, a progressive enhancement in peak sharpness was evident with increasing treatment time, indicating improved atomic ordering. The 6H and 24H samples exhibited the most intense diffraction peaks, implying superior crystallinity. In the magnified diffraction region near 2θ ≈ 43°, peaks were nearly indiscernible for the raw sample but became distinctly defined in laser-treated samples, with intensity increasing proportionally with exposure duration. These results demonstrate the crystalline enhancement induced by laser processing over time.

3.6. Raman

Raman spectroscopy equipment at Advanced Light Source, Lawrence Berkeley National Lab was used to perform the Raman measurements on the raw quartz lump silica sand.



Raman spectroscopy was performed using the system at the Advanced Light Source, Lawrence Berkeley National Laboratory, on the raw quartz lump silica sand. The resulting spectrum revealed distinct vibrational peaks at 127, 206, and 463 cm^{-1}, which are characteristic of α-quartz, confirming its presence in the analyzed quartz lump samples. While the anomalous peak at 2500 cm-1 is supposedly an overtone, appearing due to molecular excitation to the higher energy state. These overtones are not diagnostically useful IR features.

4. Conclusions and Recommendations:

Comprehensive characterization techniques, including Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, X-ray Diffraction (XRD), and X-ray Fluorescence (XRF), were employed on raw quartz lump samples to determine their elemental composition, quantify impurity levels, and identify the specific silica dioxide polymorph present. Analytical results confirmed that the raw quartz lump is primarily composed of α-quartz with significant amorphous content and approximately 12% impurity concentration by weight. Due to the coarse and heterogeneous nature of the raw quartz lumps, the material was homogenized via ball milling prior to laser processing to ensure uniform particle size distribution and compatibility with laser treatment parameters. Both raw and laser-irradiated samples were subsequently analyzed using scanning electron microscopy (SEM) to evaluate morphological changes and quantify particle size distribution. The average particle diameter decreased substantially from 124 μm in the raw sample to 56 μm following 6 hours of laser treatment, indicating a pronounced comminution effect induced by laser exposure.

The intrinsic thermal conductivity of quartz ranges from 1.35 to 2.52 W/(m·K), increasing with temperature. However, the effective thermal conductivity is further enhanced by radiative heat transfer mechanisms, with a measured 26.4% increase at 1100 K relative to intrinsic values. XRF analysis revealed that prolonged laser irradiation led to enhanced ablation of non-silica constituents, as evidenced by the increased SiO_2 weight percentage in the 24-hour treated samples. XRD patterns of both untreated and laser-processed specimens demonstrated the laser's capacity to induce structural reordering and enhance crystalline with extended treatment durations.

It is anticipated that deploying a higher-powered laser system would further augment impurity ablation efficiency, improve thermal energy transfer, and increase the overall rate of material processing compared to the current laser configuration, thereby optimizing the quality and purity of processed quartz.