

S₁. Advantages of a prism over beam splitter-based set-up for LIBS-LIF-Raman measurements

The main function of the beam splitter was to divide the beam into a different ratio. In the previous works, a 1 inch 532 nm pellicle beam splitter with a spectral window from 300-1000 nm and designed in a 60/40 ratio i.e.; 60% of the incident beam will reflect towards the sample. It is kept at an angle of 45° to the incident beam to efficiently direct the beam to the sample. But, there are different issues in choosing a beam splitter for material characterization studies. Beam splitters come in three types: plate, cube, and pellicle, and mainly consist of a partially reflective coating. All these are available in different ratios, with varying power thresholds and wavelength options. Compared to plate and cube beam splitters, pellicle one is free from ghost reflections from exit and entry surfaces but offers lower power handling and optical performance due to the thin layer of coating over it. In such cases, the requirement of higher energy for LIBS measurements of some samples to get the atomic emission lines is not possible. But high-quality coatings will eliminate ghost reflections. In our case, the coating works for only a specific wavelength i.e., 532 nm so that we cannot use it for other harmonics. But there are broadband high energy damage threshold coatings available. Since we are aiming for a portable system for real-time applications, sometimes our studies demand the use of more than one harmonic, (e.g. 266 nm for Resonance Raman, 1064 nm for fluorescing material's Raman, like tissues), to precisely analyze a particular sample. Since we are using a power-splitting beam splitter, it is non-polarizing and does not give rise to a major difference in the incident and reflected beam. The transmission curve of the 532 nm beam splitter used is shown in figure A. The transmission spectrum shows a broad transmission from 300 – 900 nm, preventing its use in certain spectral ranges.

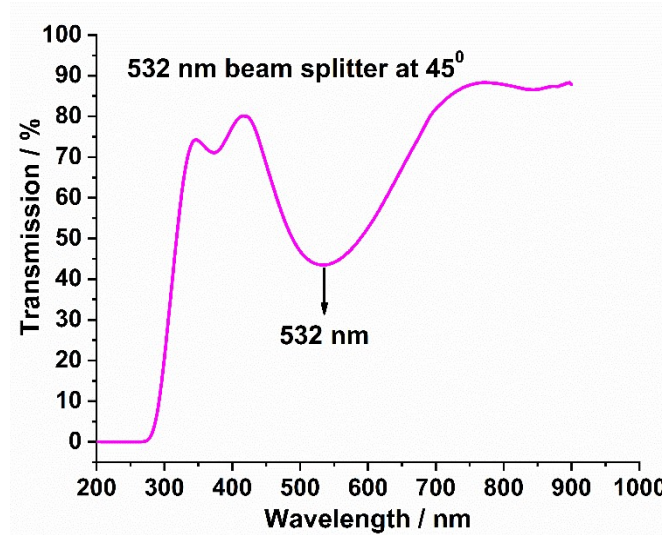


Figure A: UV-VIS spectra of the 532 nm beam splitter

But instead of using a beam splitter, a better choice will be a right-angle prism which is devoid of the aforementioned issues. Since prisms are made of solid blocks of glass rather than coated materials, they are naturally athermalized i.e., less affected by the environmental variations. They can withstand high powers, reduce the alignment issues, overall system size, cost, and general maintenance, and are independent of wavelengths used in the present studies. A prism does not split the laser beam in terms of power, rather it reflects the entire beam incident on it. The optimization of various experimental parameters has been done with standard samples and successfully employed for the identification of various samples.

S₂. LIBS-LIF-Raman measurements with ICCD coupled CT spectrograph

The conventional LIBS-LIF-Raman measurements of the natural mineral calcite were checked with thermo-electrically cooled ICCD coupled CT (Kymera 193i, Shamrock, Andor) spectrograph. It is a rugged compact system that offers superior detection capabilities for LIBS, Raman, and LIF measurements. Its high throughput, real-time monitoring, and time gating possibilities give meaningful data for interpretation. It has two interchangeable diffraction gratings with 1200 and 600 grooves/mm with a spectral range of 75 and 150 nm. For LIBS, Raman, and LIF measurements, we have used 600 grooves grating and a slit width of 100 μ m. Figure B shows the conventional LIBS-LIF-Raman spectra of the calcite sample. We have employed 532 nm excitation, 6 ns pulse width, and 10 Hz repetition rate, which is directed to the

sample surface through prism kept at 45° and a focusing lens. The energy used for LIBS is 18 mJ, and Raman-LIF 4-6 mJ.

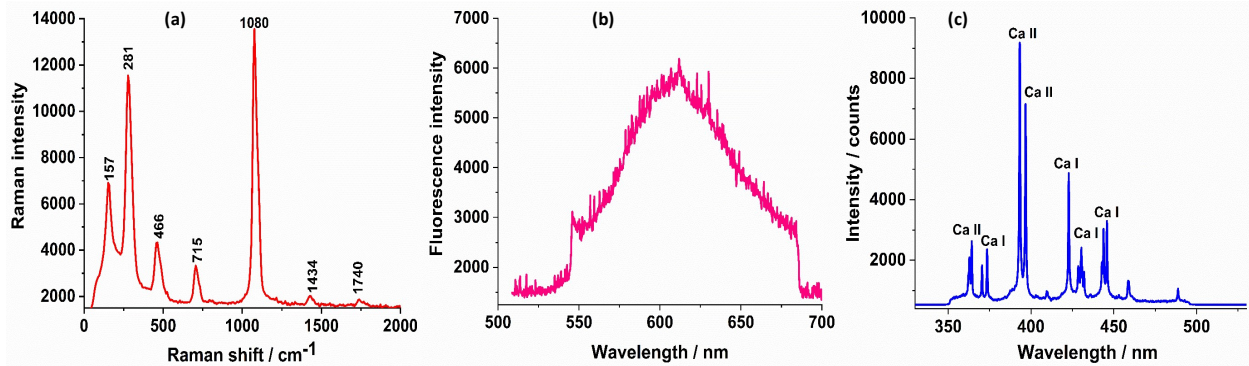


Figure B: Conventional (a) Raman (parameters: gate delay-10 ns, gate width-20 ns, energy- 4 mJ, integration time-40 s), (b) LIF (parameters: gate delay-15 ns, gate width-50 ns, energy-5 mJ, integration time-20s), and (c) LIBS spectra (parameters: gate delay-800 ns, gate width-10 μ s, energy-18 mJ, integration time-0.2s) of calcite mineral

Figure B (a) shows the Raman spectrum of calcite recorded at gate delays 10 ns keeping a gate width of 20 ns, integration time of 40 s. The Raman spectrum shows the characteristic peak of carbonate ion at 1080 cm^{-1} , corresponding to the symmetric stretching vibration of CO_3^{2-} in the crystal along with other peaks at 157, 281, 466, 715, 1434, 1740 cm^{-1} . These peaks are due to the lattice mode vibrations and antisymmetric stretching modes and very weak combination mode, respectively, except a peak at 466 cm^{-1} indicates the signature of quartz present in the sample as an impurity. Later, fluorescence background was observed in figure B(b) with an emission maximum in the 612nm region. In the calcite sample, the observed fluorescence in the orange-red region is mostly due to divalent manganese (Mn^{2+}). The LIBS spectra show the typical Ca emission lines throughout the spectral region 350-500 nm as in figure B (c). The atomic emission lines at 364.5, 370.4, 373.4, 393.38, 396.7, 422.8, 430.3, 443.65, 445.4 nm, etc. reach optimum around 700-800 ns gate delay with gate width 10 μ s, integrated over 0.2s.