



Solid-state 320 nm laser to replace HeCd laser in UV Raman spectroscopy analysis of ferroelectric perovskite thin films and heterostructures

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Laser technology has evolved significantly over the years, driven not only by advances in engineering and optics but also by increasing environmental and regulatory pressures. In particular, the European Union has initiated the phased restriction of cadmium (Cd), a highly toxic transition metal known to pose serious risks to both human health and the environment. As a result, it is becoming increasingly interesting to look for safer laser alternatives to helium-cadmium (HeCd) lasers. In this application note we demonstrate how new diode-pumped solid-state lasers can serve as a very attractive Cadmium-free alternative to HeCd lasers in demanding ultra-low frequency Raman spectroscopy analysis, by offering stable single-frequency emission at a similar UV wavelength, with in a high-quality beam and from a compact form factor.

UV lasers in Raman spectroscopy

Ultraviolet Raman spectroscopy has emerged as a powerful technique for many applications. In chemistry, biology, and pharmacy the advantages of the UV excitation include increased sensitivity and the intensity (signal to noise ratio) of the Raman spectra, resonant excitation, and elimination of fluorescence background. The fluorescence response of complex organic compounds and biological samples can be reduced by using a longer wavelength and is often completely eliminated by using near infrared excitation, such as 1064 nm. Another option is to excite Raman spectra at wavelengths below the fluorescence window by means of UV excitation. Additionally, using UV excitation can lead to a relatively large (up to 2-4 orders of magnitude) resonance amplification of the Raman signal in some samples. Also, UV radiation has a shorter wavelength than visible or infrared radiation, which allows for better spatial resolution when using micro-Raman spectroscopy for mapping molecular structures or Raman imaging.

A commonly used laser in UV Raman spectroscopy analysis is Helium-Cadmium (HeCd) lasers. HeCd lasers are gas lasers that emit in the visible and ultraviolet regions, most commonly at wavelengths of 442 nm (blue) and 325 nm (UV). Helium-Cadmium (HeCd) lasers are valued for their ability to emit stable, continuous-wave light with a narrow linewidth, high spectral purity, and excellent beam quality with a TEM₀₀ mode, making them ideal for precision applications like spectroscopy (such as Raman and fluorescence), holography, and photolithography. Their low intensity noise, long coherence length, and stable linear polarization further enhance their suitability for sensitive optical measurements. These features have made HeCd lasers a standard in scientific and industrial fields requiring high-resolution optical excitation.

The HeCd lasers, however, utilize a highly toxic and environmentally hazardous material, Cadmium, which creates regulatory, handling, and disposal issues. In addition, HeCd lasers are bulky, inefficient, require high maintenance, and have limited lifetimes. For these reasons, there is an increasing interest in looking into finding alternatives to HeCd lasers. One such alternative is diode-pumped and frequency-converted solid-state lasers at 320 nm. These lasers can offer a safer, more

efficient, more compact and more sustainable alternative to HeCd lasers. Herein, we thus focus on the advantages of UV excitation in Raman spectroscopy for characterization of nanoscale inorganic materials, in particular, wide-bandgap semiconductors and dielectrics, while demonstrating how the use of a compact diode pumped solid state (DPSS) 320 nm lasers compares to the use of a HeCd laser at 325 nm.

Raman analysis of thin-film perovskite oxide heterostructures

Complex oxides are a vast class of materials that have a wide variety of functional properties. Among these functionalities, ferroelectricity has been intensively studied over the past few decades. Ferroelectrics are a class of materials possessing a spontaneous electric polarization, which arises from the ordering of electric dipoles and can be switched between crystallographically defined directions by applying an electric field. Ferroelectric materials have been investigated for various device applications such as non-volatile memory, piezoelectric micro- and nanoelectromechanical systems, tunable microwave devices, integrated optics and photovoltaics applications. The advances of epitaxial oxide thin film deposition have rapidly moved the science and technology of ferroelectrics towards thin films and multilayer structures at the nanometer scale. Nanoscale ferroelectrics are fascinating objects from the fundamental physics point of view, since the reduction of the structural dimensions gives rise to new phenomena and properties dramatically different from those of bulk ferroelectrics.

Of central importance for understanding the fundamental properties of ferroelectrics is dynamics of the crystal lattice, which is closely related to the phenomenon of ferroelectricity. Lattice dynamics in bulk perovskite oxide ferroelectrics have been investigated for several decades using neutron scattering, far infrared spectroscopy, and Raman scattering. Raman spectroscopy is one of the most powerful analytical techniques for studying the lattice vibrations and other elementary excitations in solids providing important information about the structure, composition, strain, defects, and phase transitions. Study of lattice dynamics in ferroelectric films and heterostructures thinner than ~100 nm has been a challenging task.



A difficulty in applying conventional Raman spectroscopy for thin films of ferroelectrics and other wide-bandgap materials using visible or near-infrared excitation, is that the visible photon energy is much smaller than the bandgap. Consequently, the absorption of light is extremely weak, and the penetration depth is large, allowing light to travel through the thin film into the much thicker substrate. The much larger scattering volume of the substrate thus generates overwhelming signals in the Raman spectra. For UV excitation, the photon energy is above the bandgap of ferroelectric oxides such as SrTiO₃ or BaTiO₃, which leads to a much stronger absorption. This is illustrated in Fig. 1 showing absorption and penetration depth of visible and UV light in BaTiO₃.

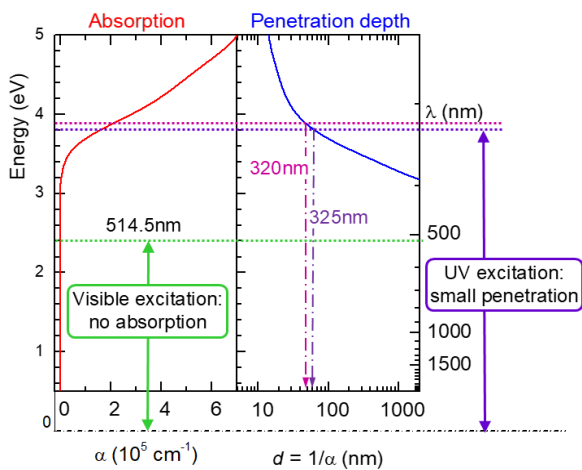


Figure 1. Schematic of the absorption coefficient α , and penetration depth d of light in BaTiO₃ as compared to the energies of the visible (514.5 nm) and UV (325 and 320 nm) photons (absorption data from Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology, New Series, Group III, Vol. 36, Subvol. A1, ed. by Y. Shiozaki, E. Nakamura and T. Mitsui, Springer, Berlin, 2001).

Therefore, using UV excitation allows probing nanometer-thin films and heterostructures because of greatly reduced penetration depth, thus avoiding the overwhelming substrate signals, which dominate the spectra of such materials measured with excitation in the visible range [Tenne et al., Science 313, 1614 (2006)]. Also, many oxide materials (such as BaTiO₃, SrTiO₃, ZnO) have bandgaps in the range 3.0–3.5 eV, and UV excitation near the bandgap can also lead to a resonance enhancement of Raman signals. This enhancement, combined with the intensity increase resulting from the ω_4 dependence of the normal Raman scattering cross-section, gives the UV another advantage over visible excitation. For bulk dielectric crystals and ceramics, the scattering volume V can be orders of magnitude larger for non-absorbing visible excitation, thus yielding larger overall scattering intensity (unless laser energy is precisely tuned into the electronic or excitonic resonance). For nanoscale films, however, V is often determined by film thickness rather than the penetration depth, so the resonant denominator and ω_4 factor lead to a significantly larger UV Raman signal from thin films of ferroelectric oxides and other wide bandgap materials compared to visible excitation.

UV excitation presents another advantage important for characterization of high temperature phase transitions in ferroelectric materials. A difficulty in measuring Raman spectra of materials at high temperatures using visible excitation is caused by continuous background due to thermal emission, which can be rather intense compared to weak and broadened Raman features. UV excitation shifts Raman spectra to much shorter wavelength range, far away from the peak intensity of thermal radiation.

Comparing solid-state 320 nm with HeCd 325 nm

Raman studies of ferroelectric oxides and many other dielectric and semiconductor materials often involve measurements of phonon lines at Raman shifts below 300 cm⁻¹, not to mention the soft phonon modes, which are usually observed below 100 cm⁻¹ (as low as 10 cm⁻¹). Therefore, effective Rayleigh scattering filtering and stray light reduction are required. In the UV range this is usually achieved by triple monochromators using subtractive double monochromators as a filter for stray light reduction. In this report, the spectra were measured with Horiba Jobin Yvon T64000 triple spectrometer equipped with a liquid nitrogen cooled multichannel charge coupled device detector optimized for UV range.

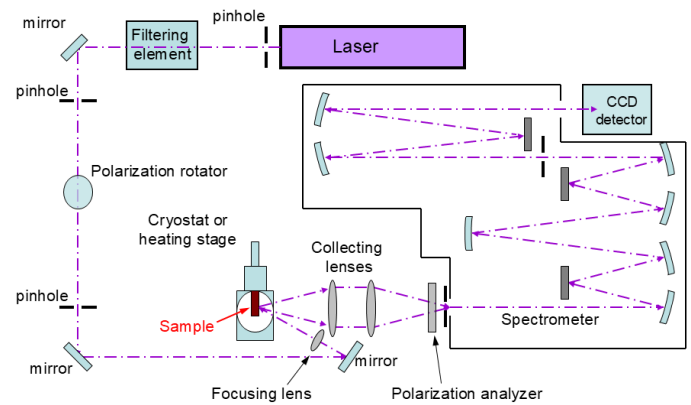


Figure 2. Scheme of the experimental setup. Optical path utilizes low optical loss high-reflectivity dielectric mirrors and fused silica lenses with antireflective coatings for minimized optical losses.

With this experimental setup, spectra of various ferroelectric oxide thin film heterostructures were measured using a 325 nm HeCd laser as the excitation source. Then with the same experimental setup a Cobolt 05-01 Zydeco laser was introduced in order to generate comparative Raman spectra with a solid-state laser. The Cobolt 05-01 Zydeco laser provides single-frequency emission at 320 nm with up to 20 mW output power in a TEM₀₀ beam. The emission has <500kHz linewidth, a very high spectral purity with SMSR of >60dB at <500 pm from the main peak (<50 cm⁻¹), a wavelength stability of <1 pm and a guaranteed lifetime of 12 months with unlimited hours of operation.



Figure 3 : Cobolt 05-01 Zydeco™ 320 nm laser with laser head (115x55x45 mm) and controller unit.

Comparative Raman spectra of a ferroelectric thin film measured with 325 and 320 nm excitation are shown in Fig. 4, using 200 nm thick $\text{Ba}_{0.45}\text{Sr}_{0.55}\text{TiO}_3$ film grown by molecular beam epitaxy on a DyScO_3 (110)-oriented substrate as an example. As one can see from the figure, the spectra, measured as close as 20 cm^{-1} from the laser line, are essentially identical, demonstrating that both lasers can be used to obtain high quality Raman data on these materials. However, the 320 nm laser has several advantages over HeCd laser. The Cobolt 05-01 Zydeco is much more compact, with the laser head measuring only 115x55x45 mm versus the 1420x146x197 mm HeCd laser of comparable emission power. The Cobolt power supply is also much more compact, and the system power consumption is less than 65 W, compared to ~700 W for a HeCd laser. Compactness is particularly beneficial in setups with space limitations, e.g. micro-Raman spectrometers utilizing interchangeable lasers. In addition, solid state lasers do not require interference filters that are needed when carrying out Raman measurements with gas lasers to filter out plasma lines.

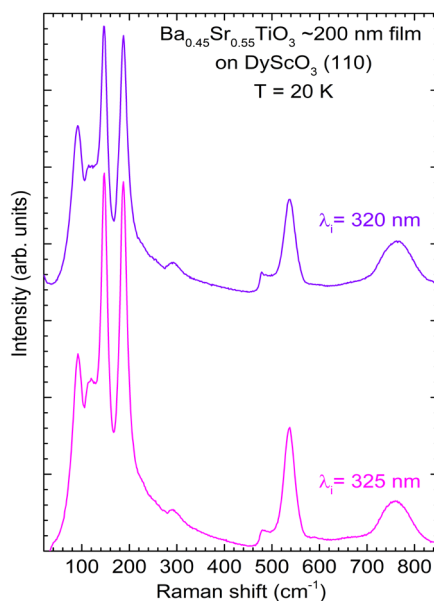


Figure 4 : Raman spectra of an epitaxial 200 nm $\text{Ba}_{0.45}\text{Sr}_{0.55}\text{TiO}_3$ film on a DyScO_3 substrate, excited at 325 nm (20 mW, HeCd-laser) and comparatively with 320 nm (20 mW, Cobolt Zydeco™).

Conclusions

Helium-Cadmium (HeCd) lasers have long been used in ultraviolet (UV) Raman spectroscopy due to their stable single-frequency emission and high beam quality. However, their reliance on cadmium—a highly toxic material—combined with their bulkiness, inefficiency, and high maintenance needs, has made them increasingly unsustainable in light of modern environmental and regulatory standards. UV Raman spectroscopy itself offers major advantages in chemistry, biology, and materials science by reducing fluorescence background, enhancing Raman signals, and improving spatial resolution, such as for nanoscale ferroelectric thin films. Here it is shown that diode-pumped solid-state (DPSS) UV lasers, such as Cobolt 05-01 Zydeco laser at 320 nm, can replace the 325 nm HeCd laser line, delivering a similar high-quality Raman spectra while offering significant benefits in compactness, efficiency, stability, and sustainability.

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