BragGrate™ Raman Filters
Volume Bragg Gratings
for Ultra-low Frequency Raman Spectroscopy
**What is Volume Bragg Grating (VBG)?**

- **VBG** is a volume hologram formed by photo-induced modulation of the refractive index (RI) of the recording media.
- **Volume hologram** – thickness is much larger than light wavelength
  - Diffraction is possible only at Bragg conditions => the light has to have the right wavelength and angle.

- Prisms and surface gratings are **conventional dispersive elements** for different angles and wavelengths
- Spectral resolving power is up to 8,000

- VBG is a dispersive element for **single wavelength and single angle**
- Spectral resolving power up to 20,000
**PTR Glass**

Photo-thermo-refractive glass is a sodium-zinc-aluminum-silicate glass doped with silver, cerium, and fluorine which provides RI modulation after exposure to UV radiation followed by thermal development.

**Volume Bragg Gratings**

- Reflecting Bragg Grating
- Transmitting Bragg Grating
- Multiplexed Bragg Grating
- Transverse Chirped Grating
- Chirped Bragg Grating
Ultra Low Frequency (ULF) Raman Spectroscopy

Low-frequency Raman is an indispensable analytical tool in multiple areas of scientific research

- Low-frequency Raman bands (lower than 50 cm\(^{-1}\)) exist in certain proteins. They are dependent upon the conformation of the protein molecule, but are relatively independent of the form of the sample, i.e., whether it is a film or a crystal.
- In amorphous glasses, most of the Raman spectra present a low frequency response called "boson peak".
- Much minerals present low frequency vibration modes, i.e. sulfur between 0 and 250 cm\(^{-1}\), or organic materials like L-Cystine between 0 and 800 cm\(^{-1}\).
- Single-wall and multi-wall carbon nanotubes exhibit radial breathing mode (RBM) vibrations in the range 150–200 cm\(^{-1}\) which are used to characterize diameter distribution and overall quality of nanotubes as well as influence of external factors.
- Quality of semiconductor multi-layered structures (superlattices) is assessed by observing folded acoustic (FA) modes in the range 0–100 cm\(^{-1}\).
- The Relaxation modes in liquids, binary mixtures and solutions, in the range 0–400 cm\(^{-1}\), help to determine their dynamic structure.

Selected applications of ULF Raman spectroscopy

- Pharmaceutical polymorphs
- LA modes of polymer
- Semiconductor lattices and nanostructures
- Material : phase/structure
- Metal Halides
- Gases
- Carbon nanotubes
- Micro, nano-crystallites
Reflecting Volume Bragg Gratings as Raman Notch Filters

- Diffraction Efficiency (DE) up to 99.99% (standard optical density: OD>3 and OD>4)
- Spectral Bandwidth (FWHM) < 5 cm⁻¹
- Angular Selectivity (FWHM) < 5 mrad
- Wavelength Range 400 nm to 2 µm (standard: 488, 514, 532, 633, 785, 1064 nm) (extended: 405, 442, 458, 473, 491, 552, 561, 568, 588, 594, 660 nm) others can be fabricated
- Grating Thickness: 2-3 mm
- Standard BNF dimensions: 11 × 11 and 12.5 × 12.5 mm² (up to 25 × 25 mm²)
- No time degradation: stable up to 400°C and any type of optical and ionizing radiation

ADVANTAGES of BragGrate™ Raman Filters

- Ultra-low frequency measurement down to 5 cm⁻¹ with single stage spectrometers
- Simultaneous measurements of both Stokes and anti-Stokes Raman bands
- No polarization dependence
- Environmentally stable, no humidity degradation
- No degradation up to 400°C
- Stable to any type of optical and ionizing radiation
Linewidth of BragGrate™ notch filter vs thin film notch filter

Spectral profiles of the narrowest thin film filter available on the market and BragGrate Notch Filter (BNF). The bandwidth of a typical BNF is about 100-200 pm, whereas bandwidth of TF filters can’t be narrower than 2-3 nm.

Optical density of single BNF is limited to about OD4 and, thus, to provide sufficient Rayleigh light suppression depending on the measurement wavelength 2 to 3 filters have to be used in sequence.

BNFs can be (optional) mounted in Ø1” round aluminum holders for easy use with standard opto-mechanical assemblies.
Demonstration of 785 nm laser line suppression by 2 BNFs. ASE background was not removed for this demonstration. The line width of the notch filters is almost identical to the linewidth of the laser and, thus, the line is rejected completely without removing the background. That is in the case of Raman measurements the line is removed without affecting ultra low frequency modes down to 5 cm⁻¹.

Demonstration of 785 nm laser line cleaning by BPF and suppression by 2 BNFs. The original (black-line) spectrum was cleaned with a thin-film bandpass filter. Typical "shoulders" are seen which correspond to the linewidth of a thin film bandpass. After cleaning the laser with BPF the "shoulders" are removed. The figure shows that the cleaned laser line can be fully suppressed by sequential positioning of 2 BNFs.
To achieve ULF Raman measurements, the laser spectral noise has to be removed as close as possible to the laser line. Standard Bandpass filters have the line width of 200-300 cm\(^{-1}\) and, thus, all spectral noise below 200 cm\(^{-1}\) would be visible in ULF Raman spectra interfering with measured Raman bands.

BragGrate™ Bandpass Filter (BPF) has the linewidth ~5 cm\(^{-1}\) (FWHM) and, thus, removes laser noise down to 5 cm\(^{-1}\) with suppression up to -70 dB.

BPF is a reflecting VBG which diffraction efficiency and other parameters are optimized for best noise removal close to the laser line.

- **Wavelength Range**: 400 nm to 2 µm (standard wavelengths: 405, 488, 514, 532, 633, 785, 1064 nm)
- **Standard BPF dimensions**: 5 × 5 × 2 mm\(^3\) (785 nm filters are typically different in size)
- **BPFs can be mounted in 1” or 0.5” mm round aluminum holders to be used with standard opto-mechanical mounts**
- **BPFs provide both spectral and spatial filtering as shown in figures below**

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Spectral filtering of laser light with BPF. Red line: spectrum of a 785 nm diode laser with ASE background. Blue line: BPF removes the ASE background in immediate vicinity of the laser line. LD light beam cleaned with BPF enabled ULF Raman measurement down to 5 cm\(^{-1}\)

Spatial filtering of laser light with BPF. Left panel: far field image of HeNe laser beam profile without cleaning. Right panel: HeNe laser beam profile after spatial filtering with BPF. At the same time the laser is spectrally cleaned to -70 dB as close as 5 cm\(^{-1}\) form the laser line.
Examples: ULF Raman measurements of L-Cystine

Ultra-low frequency measurements of L-Cystine at 4 different wavelengths: 488, 532, 633 nm (left) and 785 nm (right)

data courtesy of Horiba Jobin Yvon
Examples: ULF Raman spectrum of SiGe superlattice

Raman Shift (cm\(^{-1}\))

-80 -77 -74 -67 -64 -57 -54 -47 -44 -37 -34 -27 -24 -17 -14 -7

Raman Shift (cm\(^{-1}\))

-500 0 500

-80 -60 -40 -20 0 20 40 60 80

-83 -77 -74 -67 -64 -57 -54 -47 -44 -37 -34 -27 -24 -17 -14 -7

-83 -73 -77 83 64 67 53 57 64 73 83

Data courtesy of:
P. H. Tan, State Key Laboratory for SL and Microstr., Institute of Semiconductors, Beijing, P. R. China; K. Brunner, University Wuerzburg, Germany

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Examples: ULF Raman spectra at 5 cm\(^{-1}\) and below

ULF Raman spectrum of several layers of MoS\(_2\) flakes

Data courtesy of P. H. Tan, State Key Laboratory for SL and Microstr., Institute of Semiconductors, Beijing, P. R. China;

Data courtesy of HORIBA; measured with LabRAM HR Evolution
BragGrate™ Raman filters in work: selected publications