

# Novel volume Bragg grating notch filters for ultralow-frequency Raman measurements

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## Summary

Recent advances in volume Bragg grating (VBG) technologies have enabled development of new types of notch filters with a bandwidth of 5-10  $\text{cm}^{-1}$ . The ultra-narrow band filters made it possible for the first time to measure Stokes and Anti-Stokes lines less than 10  $\text{cm}^{-1}$  with a single stage Raman spectrometer.

## Introduction

Ultra-low frequency Raman measurements are crucial for many important applications such as nanomaterials research, pharma, and semiconductor processing. Notch filters are used in Raman spectroscopy to reject the laser line before the spectrum is measured with a spectrometer and, thus, the filter bandwidth limits the low frequency range accessible in Raman instruments. Existing thin film and holographic notch filters have the rejection band wider than 200-300  $\text{cm}^{-1}$  that sets the limits to measurable low-frequency Raman shifts. Multichannel measurements of Raman bands with frequencies very close to the excitation line (5-100  $\text{cm}^{-1}$ ) have traditionally been possible with the use of triple-stage monochromator systems [1, 2]. The presented VBG-based notch filters have the bandwidth 10-20 times narrower than other existing filters and enable ultralow frequency measurement below 10  $\text{cm}^{-1}$  with single monochromator stage systems.

## Results

Volume Bragg gratings are fabricated by holographic techniques in bulk of photo-thermo-refractive (PTR) glass [3], which is a silicate glass doped with Ag, Ce, and some other dopants. After latent image formation by UV radiation, the glass substrates are thermally developed at  $\sim 500^\circ\text{C}$  allowing formation of NaF nano-clusters responsible for the spatial refractive index modulation inside the glass matrix, typically with the grating period of 150-200 nm for such filters.

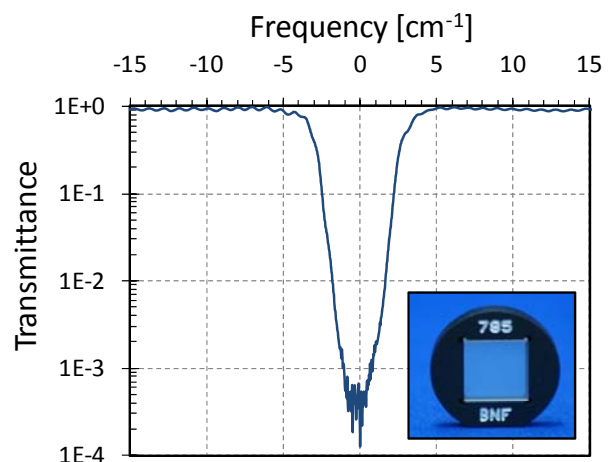


Fig. 1 Transmission spectrum of 785 nm notch filter with 6  $\text{cm}^{-1}$  bandwidth, optical density 3.5, and throughput exceeding 90%. Inset shows a photograph of 12.5x12.5  $\text{mm}^2$  filter.

Recent advances in materials and holographic recording techniques of VBGs enabled development of notch filters with unmatched characteristics, such as narrow bandwidth, high optical throughput, and high optical density (OD). For example, notch filters for 785 nm wavelength have  $6\text{ cm}^{-1}$  FWHM bandwidth, throughput 90-95%, and the OD can be as high as 5. VBG filters have no polarization dependence and can be made in the wavelength range from 450 nm to  $2\text{ }\mu\text{m}$ , however, primarily they are fabricated to match major Raman laser source wavelengths such as 488, 532, 633, 785, and 1064 nm. Fig. 1 shows a typical transmission spectrum of a 785 nm notch filter. No organic materials are used in the notch filters and, therefore, they have unlimited lifetime and outstanding environmental stability, with no humidity or light induced degradation, and can withstand temperatures up to  $450^\circ\text{C}$ . All filters used in the experiments had broadband anti-reflection coating on both sides.

The ultra-narrow notch filter performance was tested in a single stage monochromator Raman systems to gain access to Raman frequencies very close to the laser line at 488, 532, and 633 nm. LabRamHR Raman system from Horiba Jobin-Yvon was utilized for the experiments and sets of three OD3 filters at each wavelength were used to reject the corresponding laser lines. Using l-cysteine as a probe material, Stokes and Anti-Stokes bands at  $9\text{ cm}^{-1}$  were simultaneously measured with a single stage spectrometer (Fig. 2) for all three wavelengths. The cut-off frequency of the filters is  $3\text{-}4\text{ cm}^{-1}$ , thus, measurements of bands down to  $4\text{ cm}^{-1}$  are feasible and have been demonstrated.

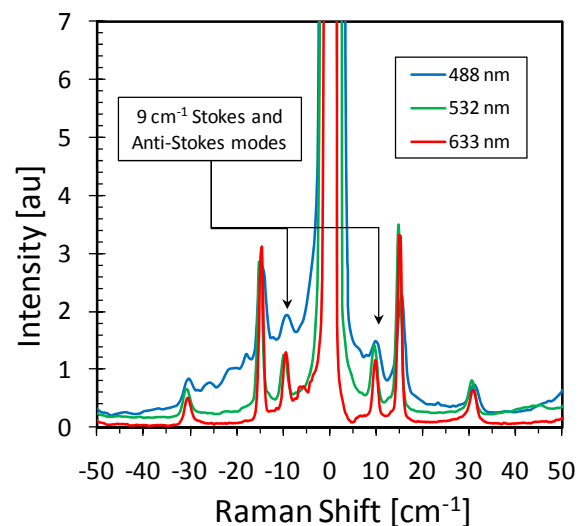


Fig. 2 Raman spectra of powdered l-cysteine measured with a single-stage spectrometer and VBG notch filters at 3 different wavelengths.

## Conclusions

We demonstrated the new type of ultra-narrow band notch filters formed in PTR glass by holographic techniques. The filters have the rejection line width 10-20 times narrower than any other notch filters. With these notch filters, simultaneous measurements of Stokes and Anti-Stokes modes below  $10\text{ cm}^{-1}$  were made possible with a single stage spectrometer Raman system.

## References

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