

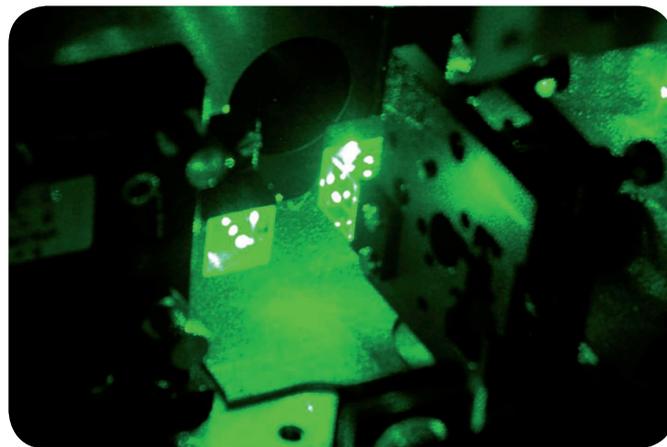
## Application Note # AN134

# Infrared Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is an important semiconductor analysis technique in material sciences as well as for research and development of optoelectronic devices such as lasers, LEDs or sensors. PL is a valuable tool to study the band structure, exciton features, sample quality or phonon modes of hetero structures (e.g. quantum wells) or bulk samples. Based on decades of experience Bruker offers powerful PL solutions with the VERTEX FT-IR research spectrometer series forming the backbone.

### Advantage of FT-IR technology

In the infrared spectral range FT-IR spectroscopy has major advantages over dispersive (e.g. grating or prism based) systems. Due to the so-called Jaquinot (or throughput) advantage [1] the sensitivity of FT-IR spectrometers is significantly higher. Thanks to the so-called Fellgett (or multiplex) advantage FT-IR combines high spectral resolution and a broad spectral range in one measurement. In contrast for dispersive systems high resolution must typically be paid with a much smaller spectral range and may require to exchange gratings etc.. In FT-IR spectroscopy spectral resolution is comfortably controlled via the software adjustable traveling distance of the moving interferometer mirror. Also the spectral accuracy of FT-IR instruments is considerably higher thanks to the usage of a precise interferometer control laser.



Keywords	Instrumentation and Software
FT-IR	VERTEX, vacuum
Photoluminescence	PL module, PLII
Semiconductors	Step-Scan
Infrared	Cryostat, pulse tube
Photoreflectance	Amplitude modulation

It should be mentioned that due to the exceptional VERTEX series sensitivity, Bruker is also number one supplier of dedicated low temperature FT-IR PL systems for quality control in Si industry (see AN M 55).

### Near Infrared Photoluminescence

For near infrared (NIR) PL Bruker offers the versatile PLII module (fig. 1): it can be adapted to the right hand side of any VERTEX FT-IR spectrometer equipped with suitable optical components in order to spectrally analyze PL. Since in the NIR atmospheric absorption (water vapor, CO<sub>2</sub>) is rather weak, a vacuum spectrometer is not necessarily required. Highest spectral resolution of  $<0.06 \text{ cm}^{-1}$  ( $<7.5 \text{ } \mu\text{eV}$ ) can be achieved with the VERTEX 80 / 80v and high resolution option, corresponding to  $\sim 0.006 \text{ nm}$  ( $0.024 \text{ nm}$ ) at a wavelength of  $1 \mu\text{m}$  ( $2 \mu\text{m}$ ). Since the PLII module has its own sample compartment, the VERTEX itself can

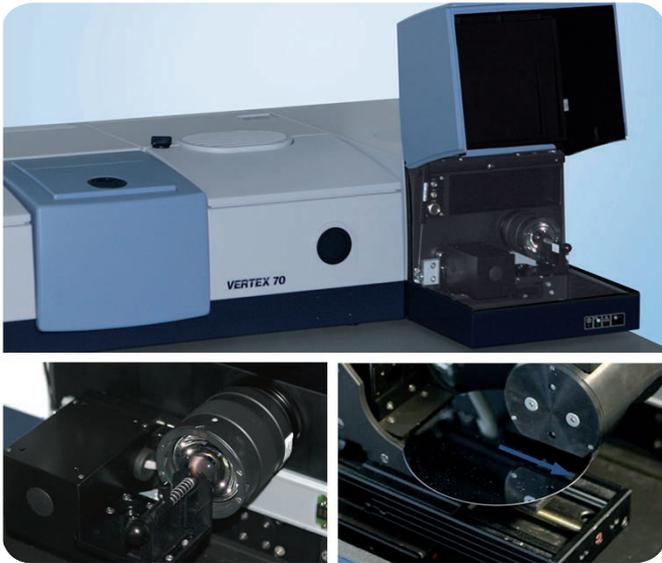


Fig. 1: Top: PII module adapted to VERTEX 70 research FT-IR spectrometer. Lower left hand side: standard glass objective with vertical sample mount. Lower right hand side: mirror objective and X-Y mapping stage for convenient horizontal sample positioning.

in addition be used for applications such as reflectance or transmittance (see FT-IR semiconductor application brochure).

The PII module can be equipped with up to two software controlled continuous wave (cw) excitation lasers. Standard wavelengths are 532 nm and 1064 nm with intensities in the order of 100 mW, others are available on request. Suitable optical laser filters are crucial and available as well. Optionally the PII module can be operated with an external customer laser instead of internal ones. For NIR PL, high gain InGaAs detectors covering a range from either 4000  $\text{cm}^{-1}$  (2.5  $\mu\text{m}$ ) or 5800  $\text{cm}^{-1}$  (~1.7) up to ~12000  $\text{cm}^{-1}$  (~0.84  $\mu\text{m}$ ) achieve excellent sensitivity as e.g. shown by the various PL spectra in fig. 2 with just a few seconds of measurement time.

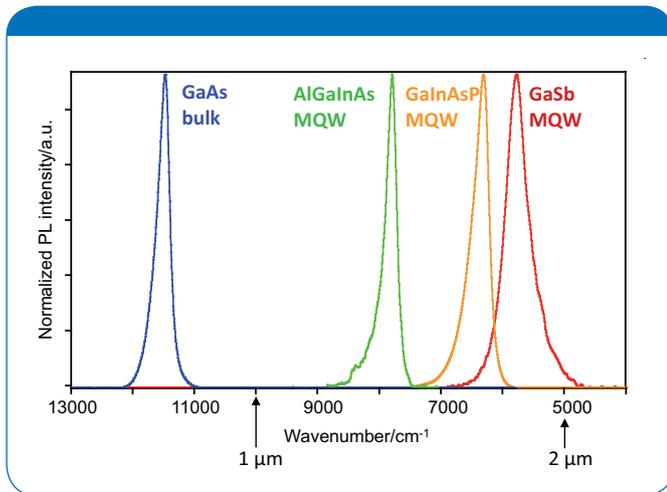


Fig. 2: NIR PL spectra of multiple quantum well samples (MQW) and GaAs bulk sample, measured with VERTEX 70, PII module, NIR/VIS beam splitter, high gain InGaAs detector and 532 nm excitation. Measurement duration per spectrum was significantly <10 seconds.

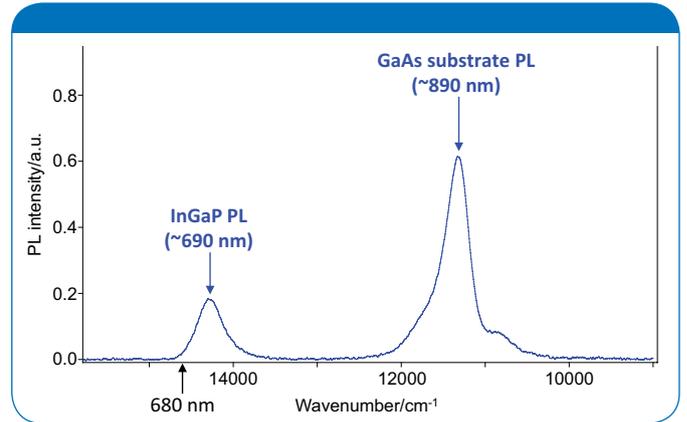


Fig. 3: NIR/VIS PL spectrum of an InGaP solar cell, measured with VERTEX 80, PII module, NIR/VIS beam splitter T502/8, dedicated Si avalanche diode and 532 nm cw excitation.

If VERTEX detector positions shall be permanently available for other applications (e.g. reflectance or transmittance), the PL detector can also be placed in the PII module. In special cases utmost NIR sensitivity can be achieved with a liquid Nitrogen cooled Ge detector.

As discussed, in the infrared spectral range FT-IR is superior to dispersive spectrometers while in the visible and ultraviolet spectral range (VIS/UV) typically the dispersive approach is of advantage. However, for customers doing mainly infrared and just occasionally VIS PL, VERTEX + PII systems can also be extended to long wave VIS range (fig. 3). For this purpose a dedicated Si avalanche diode is available, covering a range from approx. 9500  $\text{cm}^{-1}$  (~1.05  $\mu\text{m}$ ) to ~20000  $\text{cm}^{-1}$  (~500 nm). In addition the VERTEX spectrometer must be equipped with aluminum coated mirrors and a suitable NIR/VIS/UV beam splitter. Mid infrared PL below ~4000  $\text{cm}^{-1}$  (approx. >2.5  $\mu\text{m}$ ) typically requires dedicated solutions discussed in the next paragraph.

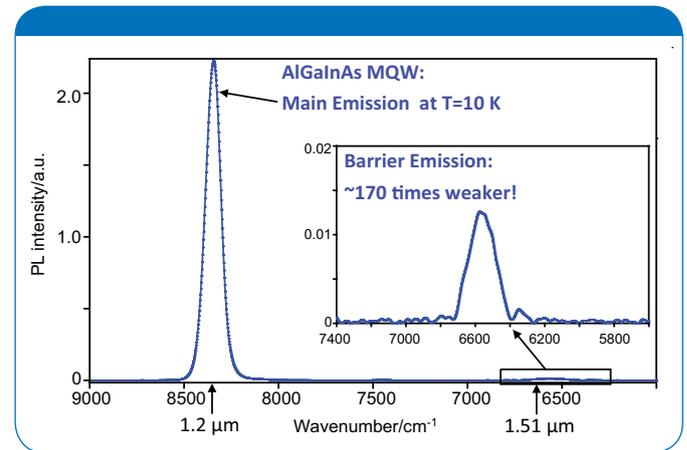


Fig. 4: Low temperature (10K) NIR PL spectrum of an AlGaInAs multiple quantum well, measured with VERTEX 70, NIR beam splitter T401/3, high gain InGaAs detector, 532 nm excitation and liquid He flow through cryostat adapted to PII module. Inset: Although measurement time was only 7 s, even the approx. 170 times weaker barrier emission was simultaneously detected.

The PLII sample compartment can be equipped with many useful and easily exchangeable accessories. E.g. a mirror objective (with video option) and an automated room temperature X-Y mapping stage are available and recommended to place the sample horizontally beneath the objective (fig. 1). For low temperature PL (fig. 4) a liquid He or N<sub>2</sub> flow through cryostat including adaption is available. Further NIR PL examples measured with the powerful combination of VERTEX and PLII can e.g. be found in [2] and [3].

### Mid Infrared Photoluminescence

For mid infrared (MIR) PL two additional challenges occur, making the application much more sophisticated. Firstly atmospheric absorption (water vapor, CO<sub>2</sub>) is significantly stronger: while in case of e.g. reflectance or transmittance the main part of atmospheric artifacts is compensated by the reference measurement, PL typically means single channel spectroscopy without reference measurement. Therefore, even under good purge conditions, the spectrum can contain strong atmospheric absorption bands as illustrated in fig. 5. Thus in order to get good quality MIR PL spectra, it is practically a must to use a vacuum FT-IR system with evacuated PL beam path.

The second challenge concerns the mid infrared 300 K background radiation surrounding us. The required high gain LN<sub>2</sub> cooled detectors are sensitive to this radiation and weak MIR PL signals can therefore completely get lost. The red curve on the right hand side of fig. 5 shows the harmful effect of background radiation, using the borderline case of an InGaAs sample emitting at ~4000 cm<sup>-1</sup> (2.5 μm).

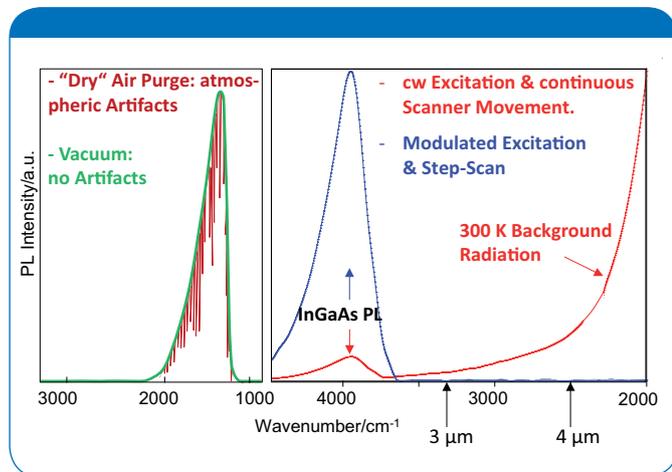


Fig. 5: Left hand side: Bad influence of atmospheric absorption (red curve) on MIR PL which can even occur for well purged spectrometers. Using a vacuum spectrometer instead, atmospheric artifacts can completely be removed (green curve). Right hand side: InGaAs PL measured with VERTEX 80v, liquid N<sub>2</sub> InSb detector, vacuum PL module and 1064 nm excitation. For cw excitation 300 K background radiation covers the MIR spectral range (red curve). With modulated excitation, step-scan and lock-in detection thermal background can be completely removed (blue curve).

Although this sample could still be measured via the standard approach, it becomes clear that for PL signals which are further in the MIR range and/or weaker, this approach (as well as subtraction of the 300K background) will finally fail.

The proper solution is to modulate the excitation laser e.g. by a chopper wheel [4, 5]: hence the PL signal will be modulated with the same frequency and can be amplified via a lock-in amplifier, while the constant thermal background contribution is blocked. Because laser modulation would interfere with the modulation created by the interferometer scanner, MIR PL typically requires step-scan operation (so-called amplitude modulation) achieving highest accuracy under vacuum conditions [6].

Fig. 6 shows the ideal MIR PL system consisting of a VERTEX 80v vacuum spectrometer and a dedicated vacuum PL module: it can either be used with external customer laser or is available with up to two preinstalled lasers. A liquid He or N<sub>2</sub> flow through or a cryogen free pulse tube cryostat is available including adaption. The PL detector requires dual channel electronics in order to send/receive the signal to/from the lock-in amplifier and to finally digitize it via integrated dual channel ADC.

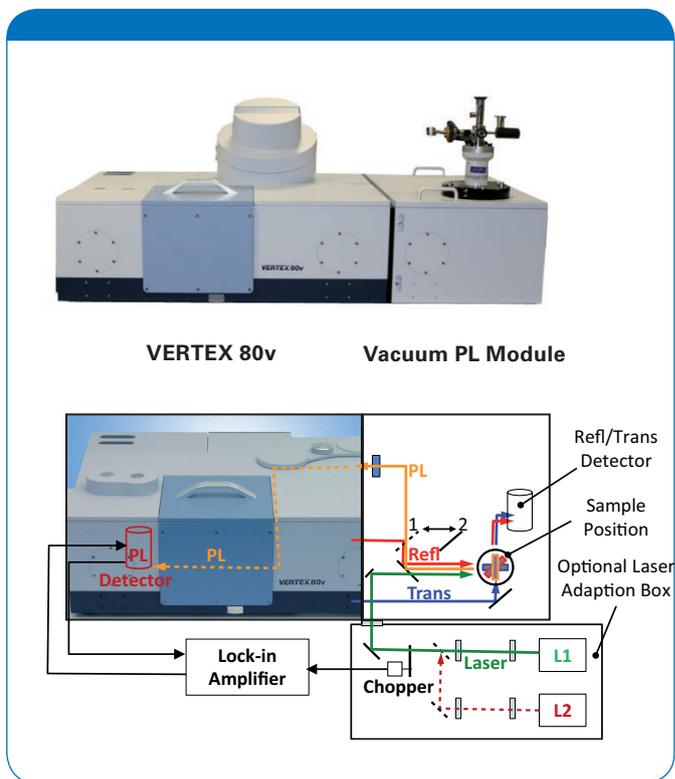


Fig. 6: Top: VERTEX 80v with vacuum PL module and LHe flow through cryostat. Bottom: sketch of vacuum PL module with laser adaption and beam paths for PL (orange), reflectance (red) and transmittance (blue). The OPUS software allows to comfortably switch between the 3 different modes.

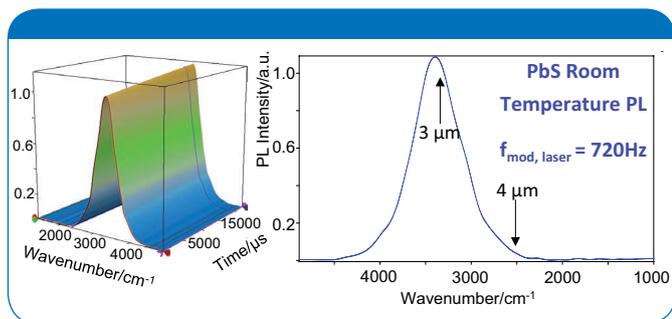


Fig. 7: Room temperature MIR PL of PbS bulk sample, measured with VERTEX 80v, vacuum PL module, modulated 1064 nm excitation, step-scan and lock-in demodulation. Left hand side: After demodulation the MIR PL spectrum is constant in time and thermal background is suppressed. Right hand side: resulting PbS MIR room temperature PL spectrum.

An example MIR PL measurement of PbS at room temperature is shown in fig. 7: after demodulation the signal is constant in time and MIR PL can be extracted without thermal background radiation.

Many scientific publications include MIR PL spectra measured with VERTEX 80v and vacuum PL modules such as e.g. [7] and [8] and a spectral range down to at least  $\sim 600 \text{ cm}^{-1}$  ( $> 16 \mu\text{m}$ ) can be reached. In the MIR spectral range the VERTEX80v high resolution option ( $< 0.06 \text{ cm}^{-1}$ , respectively  $< 7.5 \mu\text{eV}$ ) corresponds to  $0.038 \text{ nm}$  ( $0.6 \text{ nm}$ ) at a wavelength of  $2.5 \mu\text{m}$  ( $10 \mu\text{m}$ ).

The vacuum PL module also includes two additional beam paths for transmittance and reflectance (see fig. 6) with comfortable switching controlled by the OPUS software. This also allows for sophisticated measurements such as photomodulated reflectance (PR) where weak reflectance changes due to modulated excitation are analyzed in order to explore the band structure [9]. Also PR experiments are typically done in step-scan mode and require special electronics to simultaneously measure the constant and the modulated part of reflectance. Vacuum is still strongly recommended and various publications with Bruker vacuum spectrometers can be found such as e.g. [10] and [7].

## Summary

Finally it should be added that experienced customers might also be able to build their own external PL setup and use the VERTEX spectrometer only for spectral analysis. But certainly this is non-trivial and the achieved sensitivity as well as the usability is at least questionable. With the PLII module adapted to a VERTEX series spectrometer, comfortable NIR PL measurements with highest sensitivity are readily available. Vacuum spectrometers such as the VERTEX 80v with dedicated vacuum PL module open the door to sophisticated and challenging applications like MIR PL or photomodulated reflectance.

## References

- [1] P.R. Griffiths, "Fourier Transform Infrared Spectroscopy", 2nd edition, Wiley-Interscience (2007)
- [2] T. Gründl et al., "GaInAsN growth studies for InP-based long-wavelength laser applications", Journal of Crystal Growth 311 (2009) 1719–1722
- [3] A. Jaffrès et al., "Photon management in La<sub>2</sub>BaZnO<sub>5</sub>: Tm<sup>3+</sup>, Yb<sup>3+</sup> and La<sub>2</sub>BaZnO<sub>5</sub>: Pr<sup>3+</sup>, Yb<sup>3+</sup> by two step cross-relaxation and energy transfer", Chemical Physics Letters 527 (2012) 42–46
- [4] S. Sauvage et al., "Midinfrared unipolar photoluminescence in InAs/GaAs self-assembled quantum dots", Physical Review B Volume 60 Number 23 (1999), 15589-15592
- [5] J. Shao et al., "Modulated photoluminescence spectroscopy with a step-scan Fourier transform infrared spectrometer", Review of Scientific Instruments 77 (2006)
- [6] C.J. Manning and P.R. Griffiths, "Noise Sources in FT-IR Spectrometry", Applied Spectroscopy Volume 51 Number 8 (1997), 1092-1101
- [7] M. Motyka, "Fourier Transformed Photoreflectance and Photoluminescence of Mid Infrared GaSb-Based Type II Quantum Wells", Applied Physics Express 2 (2009), 126505
- [8] D. Stange et al., "Optical Transitions in Direct-Bandgap Ge<sub>1-x</sub>Sn<sub>x</sub> Alloys", ACS Photonics (2015)
- [9] T.J.C. Hosea et al., "A new Fourier transform photomodulation spectroscopic technique for narrow band-gap materials in the mid- to far- infra-red", Physica Status Solidi (a) Volume 202 Issue 7 (2005), 1233-1243
- [10] Ma Li-Li et al., "Spectral Resolution Effects on the Lineshape of Photoreflectance", Volume 28 Number 4 (2011), 047801

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