

# Raman Spectra of GaP Grown from a Non-Stoichiometric Ga Melt

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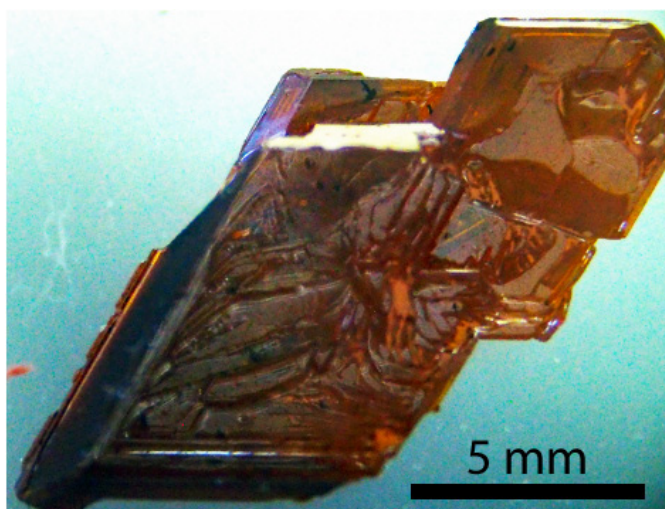
## Abstract

In this short contribution, we show the Raman spectra of gallium phosphide (GaP) grown from a non-stoichiometric Ga melt. For comparison, we also used a GaP wafer with a (100) orientation produced using the Czochralski method. The characteristic first-order and second-order Raman bands of GaP grown from a non-stoichiometric Ga melt are presented.

## Introduction

Gallium phosphide (GaP) is a III-V semiconductor and crystallizes in the thermodynamically stable cubic zinc blende structure with the lattice constant  $a = 5.45\text{\AA}$  and has an orange-red color. GaP melts at  $1470\text{ }^\circ\text{C}$  under a phosphorus pressure of 300 bar. Gallium phosphide has been used in the manufacture of low-cost red, orange, and green Light-Emitting Diodes (LEDs) with low to medium brightness since the 1960s. Hadamovsky [1] gives the principal properties of GaP and other III-V semiconductors and technologies for the production of this material.

## Sample Material




**Figure 1:** GaP single crystal platelet grown from a non-stoichiometric Ga melt (A-side).

The GaP single crystals were grown from a non-stoichiometric gallium (Ga) melt. This melt is composed of semiconductor-pure gallium and 10% GaP powder each. The closed

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quartz glass ampulla was heated for 1 hour at 1150 °C and, after that, cooled with a velocity of 30 °C/hour. While doing so, lamellose single GaP crystals grow swimming on the Ga surface (Tirpitz et al. [2]) - Figure 1. The single crystal platelets have different-looking surfaces: smooth at the part that peeps out of the Ga-melt and rough on the underside. Traditionally, the shiny side is called the A- or Ga side, and the rough side is the B- or phosphorus side.

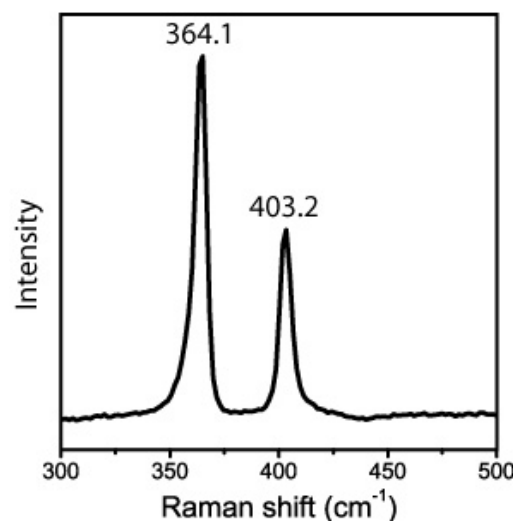
### Methodology: Raman Spectroscopy

We use the Raman spectroscopy here to characterize GaP grown from a non-stoichiometric Ga melt, which shows growth- and orientation-related differences. For the study of the GaP samples, we use the Raman spectrometer EnSpectr R532 combined with the Olympus BX43 microscope both for transmitted and reflected light and equipped with a rotating stage and polarizers (for parallel and perpendicular positions). Note here that the incident laser light is always polarized - in our case, N - S Tuschel [3]. Generally, we used an Olympus long-distance 40x objective lens for the studies. All measurements are the mean of 13 measurements taken in steps of 30° during azimuthal rotation.

As references, we applied a water-clear diamond crystal from Brazil ( $1331.63 \pm 0.60\text{cm}^{-1}$ ) and a semiconductor-grade silicon single-crystal ( $520.70 \pm 0.15\text{cm}^{-1}$ ). For this study, we generally used laser energies of  $\leq 30\text{mW}$  on the sample for the studies.

### Results

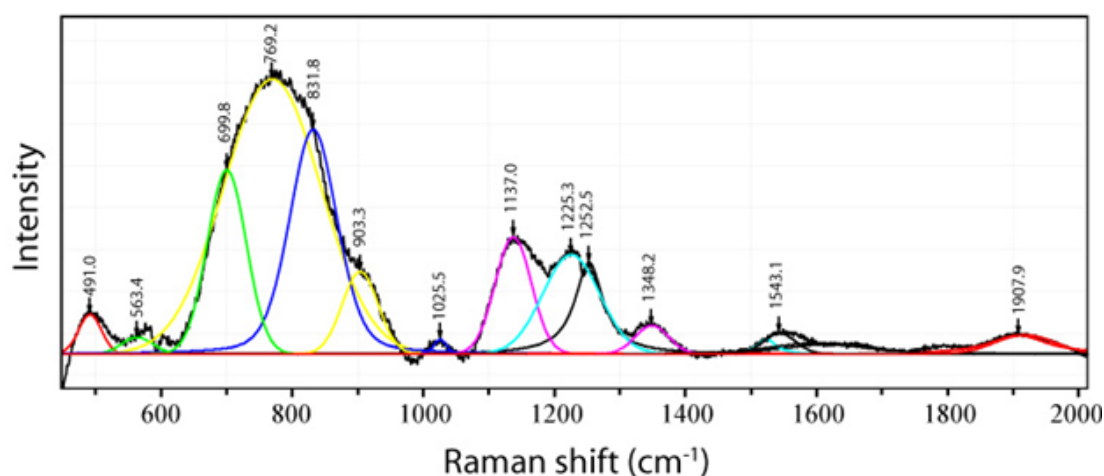
Generally, GaP crystallized from the non-stoichiometric melt as lamellose single GaP crystals with (111) orientation. The prominent Raman bands of the A-side in the first order range are  $364.1 \pm 0.01\text{cm}^{-1}$  ( $n = 14$  determinations) and  $403.2 \pm 0.1\text{cm}^{-1}$  ( $n = 14$ ) - Figure 2.



**Figure 2:** First-order Raman spectrum of GaP from the non-stoichiometric Ga melt (A-side).

The Full Width at Half Maximum (FWHM) of both main Raman bands (363 and 403) is  $6.40 \pm 0.05$  and  $6.29 \pm 0.06\text{cm}^{-1}$ , respectively. The intensity ratio is constant:  $I(364)/I(403) = 2.32$ . Other bands are very weak. For the B-side, we have obtained  $363.9 \pm 0.13$  and  $403.5 \pm 0.15\text{cm}^{-1}$  with the FWHM of  $6.70 \pm 0.06$  and  $7.49 \pm 0.63\text{cm}^{-1}$  and intensity ratio  $I(364_{\text{B}})/I(403_{\text{B}}) = 1.93$ . There are only minimal differences between both (111)-planes. The FWHM is a little bit larger for the B-side Raman bands.

Opposite to the first-order range with only a tiny number of Raman lines, the second-order Raman bands, however, are numerous. Hobden and Russell (cited in Krishnan [4]) identified 17 peaks. In the case of GaP, crystallized from the non-stoichiometric melt, we have found 12 relatively strong bands in the range of  $450\text{--}2000\text{cm}^{-1}$ . Figure 3 gives an idea about lines in the second-order range. Generally, the intensity of these lines is significantly lower than the first-order Raman bands - about 10% from the  $364\text{cm}^{-1}$  band.



**Figure 3:** Second-order Raman spectrum of GaP grown from the non-stoichiometric Ga melt (A-side). The bands around  $1200\text{cm}^{-1}$  are third-order Raman bands.

In Table 1, the primary data of the measured Raman spectrum of GaP from the non-stoichiometric Ga melt are compiled (simplified) - mean of 13 measurements.

**Table 1:** Observed Raman band, modes, and relative intensities of GaP grown from the non-stoichiometric Ga melt.

Raman Band (cm <sup>-1</sup> )	Mode	Relative Intensity	Remark
<b>A-side</b>			
76.0	$\nu_4$	s	First order
107.4	$\nu_4$	s	First order
206.9	$2\nu_4$	m	Second order
364.1	$\nu_1$ (TO)	vs	First order
403.2	$\nu_2$ (LO)	vs	First order
491.4	$\nu_1 + \nu_2$	w	Second order
708.8	$2\nu_3$	m	Second order
778.3	$2\nu_2$	m	Second order
896.6	?	w	Second order
<b>B-side</b>			
84.9	$\nu_4$	s	First order
364.0	$\nu_1$ (TO)	vs	First order
404.0	$\nu_2$ (LO)	vs	First order
715.0	$2\nu_3$	w	Second order
778.0	$2\nu_2$	w	Second order

TO - Transverse Optical, LO - Longitudinal Optical, vs - very strong, s - strong, m - medium, w - weak.

According to our and Dobrovolsky et al. [5] studies, the strong bands dominate the 320-420cm<sup>-1</sup> spectral range of the GaP Raman spectrum.

### Interpretation

(100) oriented GaP wafers grown by the Czochralski method show in the first-order range only one very strong Raman band at 405.5 ± 0.04cm<sup>-1</sup> (n = 12). The other bands (73.0, 209.3, 364.6cm<sup>-1</sup>) in the first-order range are very weak. Opposite to the Raman bands of the (111)-oriented GaP crystals, the prominent Raman bands in the second-order range are sharp: 718 ± 10.02 and 783.61 ± 0.94cm<sup>-1</sup> with the FWHM of 17.19 ± 7.03 and 16.02 ± 0.94cm<sup>-1</sup> respectively.

We see a strong dependence on the Raman fundamentals from the orientation of the GaP crystals: (111) vs. (100).

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