Zinc germanium phosphide (ZGP) has outstanding fundamental properties as a mid-IR nonlinear crystal. It is especially suitable for high average power applications throughout the infrared region. The large nonlinear coefficient of ZGP, which is approximately 160 times that of KDP, makes it one of the most efficient nonlinear crystals known.

Recent improvements in growth of ZGP at INRAD have led to the ready availability of large (>25mm), high quality crystals with low absorption in the infrared. Improved growth techniques have led to a dramatic reduction in the near infrared absorption. Today, INRAD crystals typically have an absorption coefficient, $\alpha$, that is less than 0.1cm$^{-1}$ in the 1.9µm to 2.6µm region and below 0.03cm$^{-1}$ from 2.6µm to 8.4µm. In particular, at $\lambda=2.05\mu$m, $\alpha=0.08$ cm$^{-1}$ (for the o-ray).

A typical transmission spectrum of a ZGP crystal 14mm thick is shown in Figure 1, from which one can see the fundamental cut-off and the region of multi-phonon absorption between 8.4 and 12µm. Insert 1 in Figure 1 shows the absorption coefficient, $\alpha$, from 0.5 to 2.5µm, while Insert 2 gives the reflectivity of an AR coated ZGP crystal cut for a 2.09µm-pumped OPO.

ZGP nonlinear optical elements produced at INRAD operate over a temperature range of -40 and +180°C.

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Sellmeier Equations

[Kato-97, Ref. 7]

\begin{align*}
n_o^2 &= 9.7465 + \frac{0.7096}{\lambda^2} - 0.00276 \cdot \lambda^2 \\
n_e^2 &= 10.0039 + \frac{0.7205}{\lambda^2} - 0.00277 \cdot \lambda^2
\end{align*}

[Bhar-87, Ref. 8]

\begin{align*}
n_o^2 &= 4.4733 + \frac{5.26576 \cdot \lambda^2}{\lambda^2 - 0.13381} + \frac{1.49085 \cdot \lambda^2}{\lambda^2 - 662.55} \\
n_e^2 &= 4.63318 + \frac{5.34215 \cdot \lambda^2}{\lambda^2 - 0.14255} + \frac{1.45795 \cdot \lambda^2}{\lambda^2 - 662.55}
\end{align*}

[Barnes-98, Ref. 9]

\begin{align*}
n_o^2 &= 4.64467 + \frac{5.10087 \cdot \lambda^2}{\lambda^2 - 0.13656} + \frac{4.27777 \cdot \lambda^2}{\lambda^2 - 1653.89} \\
n_e^2 &= 4.71539 + \frac{5.26358 \cdot \lambda^2}{\lambda^2 - 0.14386} + \frac{2.37310 \cdot \lambda^2}{\lambda^2 - 1000.82}
\end{align*}

[Khosh-98, Ref. 10]

\begin{align*}
n_o^2 &= 4.61511 + \frac{5.12798 \cdot \lambda^2}{\lambda^2 - 0.13624} + \frac{2.16936 \cdot \lambda^2}{\lambda^2 - 900} \\
n_e^2 &= 4.69874 + \frac{5.27924 \cdot \lambda^2}{\lambda^2 - 0.14339} + \frac{2.09861 \cdot \lambda^2}{\lambda^2 - 900}
\end{align*}

Refractive Indices and their Temperature Dependencies

\begin{table}
\begin{tabular}{|c|c|c|c|c|}
\hline
\(\lambda\), \(\mu\)m & \(n_o\) & \(n_e\) & \(dn_o/dT\) \(10^6\) & \(dn_e/dT\) \(10^6\) \\
\hline
2.05 & 3.1478 & 3.1891 & 14.3 & 15.3 \\
2.79 & 3.1333 & 3.1744 & 15.5 & 16.1 \\
5.30 & 3.1136 & 3.1547 & 14.8 & 15.8 \\
10.6 & 3.0729 & 3.1143 & 15.3 & 16.7 \\
\hline
\end{tabular}
\end{table}

Laser Damage Threshold

\begin{table}
\begin{tabular}{|c|c|c|c|}
\hline
\(\lambda\), \(\mu\)m & Pump Regime & Laser Damage Threshold \\
\hline
2.79 & 150 ps & 30 GW/cm\(^2\) \\
5.0 & cw & 0.25 MW/cm\(^2\) \\
10.6 & 2 ns & 1 GW/cm\(^2\) \\
10.6 & cw & 0.2 MW/cm\(^2\) \\
\hline
\end{tabular}
\end{table}

* These are typical laser damage values reported in the literature. Inrad does not offer warranty on optically damaged crystals.

Figure 1. Optical transmission of INRAD uncoated ZGP single crystal 14mm thick. Insert 1 gives the absorption coefficient in the region of 0.5 - 2.5\(\mu\)m. Insert 2 shows the reflectivity of a ZGP OPO crystal AR coated for 2.09/3-5\(\mu\)m.
**Applications**

ZGP is a very promising material for applications such as SHG, SFG, OPO, and OPG/OPA in the mid-infrared region.

**Optical Parametric Oscillators (OPOs)**

ZGP is an excellent OPO material in the mid-IR. Type I and type II OPO phase-matching curves are presented in Figure 2 for two typical pump wavelengths. The Sellmeier equations of Barnes and Ghosh predict the phase-matching properties for the $\lambda \sim 2 \mu m$ pump application shown here; the Kato97 and Bhar87 data bracket the OPO behavior for the $\lambda = 2.8 \mu m \sim 3.0 \mu m$.

Broad tunability of ZGP OPOs is made possible by the wide availability of pump sources and the broad phase-matching characteristics and broad spectral transmission of ZGP crystals. Pump wavelengths for ZGP OPOs generally have been longer than 1.8 $\mu m$ due to concern about absorption at shorter wavelengths. The output wavelength of a ZGP-based OPO is usually changed by angular tuning of the crystal and, to a smaller extent, by adjustment of the crystal temperature.

Erbium or Holmium solid state lasers ($2 \mu m < \lambda < 3 \mu m$) can be used to pump ZGP OPOs to achieve continuous tunability in the 3-12 $\mu m$ spectral range. Other IR coherent sources can be employed as well, including LiNbO$_3$ and KTP-based OPOs.

Efficient and high average power mid-IR OPOs built on the basis of ZGP crystals supplied by INRAD have been reported. In the most powerful mid-IR OPO, reported by Cheung et al., a type I ZGP OPO was pumped at 2.13 $\mu m$ using a KTP OPO. The ZGP OPO output, tunable between 3.7 and 4.8 $\mu m$, achieved an average output power of 22 W. Phua demonstrated a coupled tandem OPO in which a second ZGP OPO was placed within the resonator of the first KTP OPO (pumped at 1.064 $\mu m$). The system had an overall slope efficiency of 35% and was tunable between 2.7 and 8 $\mu m$. A ZGP OPO with wide mid-IR tunability has been demonstrated recently. The OPO was pumped by 100 ns erbium laser pulses at $\lambda = 2.93 \mu m$ and yielded output continuously tunable from 3.8 to 12.4 $\mu m$ (type I) and from 4 to 10 $\mu m$ (type II phase-matching). The OPO pump threshold was less than 1 mJ in the whole 4-12 $\mu m$ range of the output, and the quantum conversion efficiency reached 35%.

**Second Harmonic Generation**

ZGP permits only Type I SHG phase-matching. A number of papers have reported the development of ZGP-based SHG for CO$_2$ lasers. At pump wavelengths near 9.6 $\mu m$, a conversion efficiency of 8.1% has been demonstrated by Mason for doubling of a pulsed CO$_2$ laser ($\tau = 100$ns). With shorter pulses ($\tau = 2$ns), the external SHG conversion efficiency can be as high as 49% ($\lambda = 9.52 \mu m$).

For Type I phase-matching, the effective nonlinearity is $d_{eff} = d_{36} \sin 2\theta$. With increasing wavelengths from 9.5 to 10.6 $\mu m$, the phase-matching angle $\theta$ increases from ~62° to ~78° resulting in a more than 2-fold reduction in the effective nonlinearity and a lower SHG efficiency. In addition, multi-phonon absorption in the 9.5-11 $\mu m$ region adds to the extinction of the pump irradiation. While multi-phonon absorption is a fundamental phenomenon and cannot be eliminated, SHG conversion efficiency can be improved to some extent by heating the crystal. ZGP also can be used for efficient SHG of CO lasers ($\lambda = 5.2-6.3 \mu m$, $\theta \approx 48^\circ$).

**Fourth Harmonic Generation (FHG)**

Fourth harmonic generation of the CO$_2$ laser has been achieved using two ZGP crystals -- one as a frequency doubler, another as a fourth harmonic generator ($\theta \approx 48^\circ$). An external conversion efficiency of 5% to 7% of the fourth harmonic with respect to the fundamental has been reported.

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**Figure 2.** Type I and Type II OPO tuning curves: a) pumped at 2.09 $\mu m$ (Ho:YAG laser); refractive index data taken from [Barnes 98, Ref. 9], solid line, and [Ghosh 98, Ref. 10], dashed line. b) pumped at 2.8$\mu m$ (Er,Cr:YSGG laser); refractive index data from [Kato 97, Ref. 7], solid line, and [Bhar 87, Ref. 8], dashed line.
**Sum Frequency Generation (SFM)**

ZnGeP$_2$ crystals can be used for mid-IR up-conversion of CO$_2$ laser light into the near IR range through phase-matched mixing with 1.06µm radiation.\[10\] Additionally, CO$_2$ laser radiation can be sum frequency mixed with CO laser light to produce wavelengths near 3.5µm.\[19\]

**Optical Parametric Generator/Amplifier (OPG/OPA)**

Traveling wave optical parametric generators and amplifiers, which have no resonating cavities, have been demonstrated using ZGP crystals that are pumped by picosecond\[21,22,23\] and by femtosecond\[24\] laser pulses.

Due to its exceptionally high optical nonlinearity, ZGP has the lowest known traveling wave OPG threshold for psec pulses (~90 MW/cm$^2$). Type I generation over the range of 3.9-10 µm and type II generation over the ranges of 6-10µm and 3.9-5.1µm were achieved using Er:YAG and Er:YSGG laser pumps ($\tau$=100ps), with an OPG quantum efficiency up to 17.6%.\[21,22\] A femtosecond OPG, with an idler of 6-8µm, has been demonstrated in a 2mm ZGP crystal with a pump near 2µm.\[24\]

**Ordering Information**

All crystal growth, orientation, fabrication, polishing and testing of ZGP at INRAD is done at one site, so that you are assured of complete traceability and satisfaction with every crystal that you purchase.

**Sizes**

Standard cross sections are 6 x 8mm and 8 x 12mm and crystal lengths are 12 to 25mm. Other cross sections and lengths are available on request.

**Orientation**

For OPO applications, please specify Type I or Type II, and the phase match angle, $\theta$. Orientations of finished crystals are accurate to within 0.5 degrees.

**Finishing**

Please specify the overall optical wedge desired for the finished crystal. Crystals can be fabricated with a 30 arcminute wedge in the non-tuning direction to limit etaloning effects. If no wedge is requested, parallelism can be held to 3-5 arcminutes. Scratch/dig is 10/5.

**Coatings**

OPO crystals can be AR coated. Please specify pump wavelength and tuning wavelength regions and desired reflectivity values. For SHG crystals specify fundamental wavelength.

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**Literature Cited**

1. Data measured at INRAD, Inc.

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