中国激光

大口径超低吸收系数中红外磷锗锌晶体与器件制备

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摘要　光参量振荡(OPO)技术是目前实现全固态可调谐高功率 3～5 μm 中红外激光的主流方案，其核心是红外非线性光学晶体，晶体品质决定红外激光功率水平。磷锗锌($\mathrm{ZnGeP_2}$，ZGP)晶体性能优异，被称为“中红外非线性光学晶体之王”，但在 0.7～2.2 μm 附近存在异常的光学吸收带，这阻碍了 ZGP OPO 功率的进一步提升。针对这一问题，采用自制的梯度冷凝炉，结合超低梯度冷凝技术，生长出 3.8～5.0 cm 大尺寸 ZGP 单晶，通过定向、切割、退火、抛光、镀膜等处理后，成功实现了多种规格 OPO 器件的生产，最大器件尺寸达 30 mm×30 mm×40 mm，器件在波长 2.09 μm 和 1.064 μm 处的吸收系数分别低至 0.015 $\mathrm{cm^{-1}}$ 和 0.4 $\mathrm{cm^{-1}}$。采用单块超低吸收 ZGP OPO 器件，实现了 3～5 μm 高功率中红外激光输出，功率达 107 W，斜率效率为 75%，光光效率为 61.8%，光束质量(M^2)为 3.1 左右。

关键词　激光技术；中红外非线性光学晶体；$\mathrm{ZnGeP_2}$ 单晶；超低梯度冷凝法；高功率中红外激光

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可调谐全固态中红外激光在激光手术、大气监测和光电对抗等方面具有重要应用[1-6]，红外非线性光学晶体器件是核心部件，其质量将直接决定红外激光功率水平。目前已经商用的红外非线性光学晶体只有 $\mathrm{ZnGeP_2}$、$\mathrm{AgGaS_2}$、$\mathrm{AgGaSe_2}$ 和 GaSe 等为数不多的几个，其中 $\mathrm{ZnGeP_2}$ 晶体的性能最为优异，被称为“中红外非线性光学晶体之王”。磷锗锌($\mathrm{ZnGeP_2}$，ZGP)晶体在 0.7～2.2 μm 处存在异常的光学吸收带且该吸收带与光参量振荡(OPO)泵浦波长交叠，严重影响输出功率和转换效率。在实践中，研究者发现用热退火结合电子束辐照，可以部分解决 ZGP 晶体异常吸收的难题[7-8]，但电子束穿透深度有限(<3 mm)，器件厚度仅仅限于 6 mm，很难制备大口径器件。此外，Zawilski 等[9]发现较大尺寸晶体可以降低光学吸收。因此，探索有效降低晶体光学吸收的处理方法并改进生长工艺以制备更大尺寸的 ZGP 晶体是目前研究的重点[10-12]。本课题组采用自制的梯度冷凝炉，通过提纯原料、严格控制多晶料化学计量比，并结合后处理等改进工艺，在温场超微梯度(0.5～1.0 ℃/cm)以及微凸生长界面下，大幅度提高了 ZGP 晶体的品质，降低了晶体的缺陷，使得 0.7～2.2 μm 范围的异常光学吸收大幅度降低，加工出的 ZGP 器件在 1.064 μm 处的吸收系数仅仅为 0.4 $\mathrm{cm^{-1}}$，在 2.09 μm 处的吸收系数低至 0.015 $\mathrm{cm^{-1}}$。目前生长的 ZGP 单晶最大直径为 5 cm，成晶率大于 95%，通过定向、切割、抛光和镀膜等处理，实现了多种规格 OPO 器件的小批量化生产，由于无电子束穿透深度的限制，器件的最大尺寸可达 30 mm×30 mm，这种大口径超低吸收系数器件的成功研制为高功率大能量中红外光源的实现打下了很好的基础[12]。

图 1 为本研究组采用超低梯度冷凝法生长的 ZGP 晶体以及制备的 ZGP OPO 器件。图 1(a)和图1(b)分别为水平梯度冷凝法(HGF)和垂直梯度

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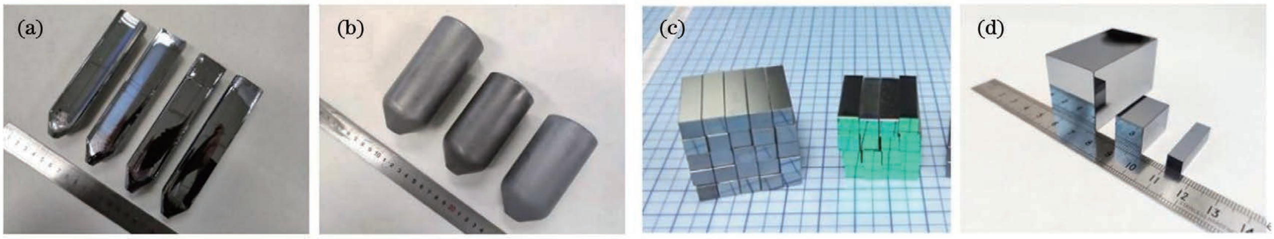

图 1　超低梯度冷凝法生长的 ZGP 单晶与制备的 ZGP OPO 器件。(a)水平梯度冷凝法生长的晶体；(b)竖直梯度冷凝法生长的晶体；(c)常规的 ZGP OPO 器件；(d)大口径的 ZGP OPO 器件

Fig. 1　ZGP single crystals grown by freezing method with ultralow gradient and ZGP OPO devices. (a) Crystals grown by HGF; (b) crystals grown by VGF; (c) regular ZGP OPO devices; (d) large aperture ZGP OPO devices

冷凝法(VGF)生长的 3.8～5.0 cm 大尺寸 ZGP 单晶，图 1(c)和图 1(d)分别为小批量常规的 ZGP OPO 器件(尺寸为 6 mm×6 mm×25 mm)和大口径的 ZGP OPO 器件(最大尺寸为 30 mm×30 mm×40 mm)。

图 2 为常规电子辐照处理方法和超低梯度冷凝法获得的器件在 0.85～2.50 μm 范围内的吸收系数对比情况。在 1.064 μm 处，前者的吸收系数高达 1.8 cm^{-1}，而后者仅仅为 0.4 cm^{-1}；在 2.09 μm 处，前者的吸收系数为 0.04 cm^{-1}，后者的吸收系数低至 0.015 cm^{-1}，两者差异减小。泵浦源波长处吸收系数的大幅下降可以大大减轻高功率泵浦下的热效应，有利于转化效率和光束质量的提升。

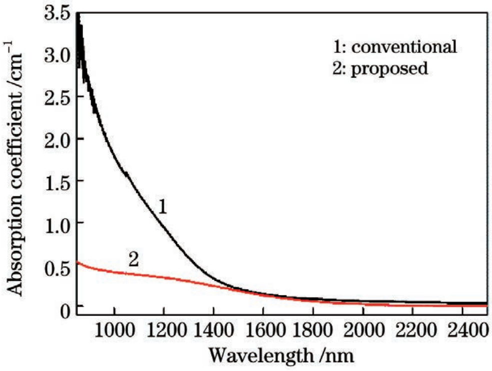

图 2　不同方法制备的 ZGP OPO 器件的吸收系数比较

Fig. 2　Absorption coefficient comparison of ZGP OPO devices prepared by different methods

图 3 为超低梯度冷凝法制备的 ZGP 器件的 OPO 激光实验结果，其中 M_x^2 为 x 方向的光束质量因子，M_y^2 为 y 方向的光束质量因子。泵浦光为 20 kHz 的 2.09 μm Ho∶YAG 脉冲激光器，晶体器件尺寸为 6 mm×6 mm×30 mm，当泵浦光功率为 173 W 时，中红外激光的输出功率为 107 W，斜率效率为 75%，光光效率为 61.8%，光束质量(M^2)为 3.1 左右。可见由于晶体吸收系数的降低，在保证光束质量的情况下，仅用单块 ZGP 器件就能实现大于 100 W 高效高功率的中红外激光输出。

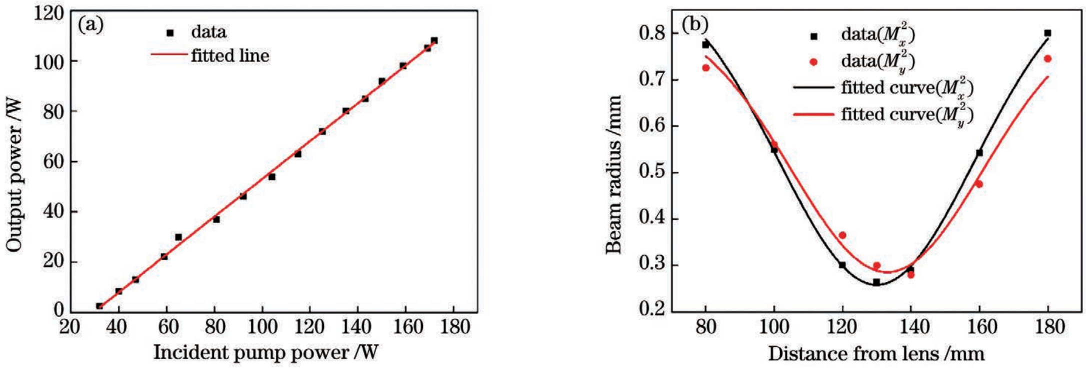

图 3　ZPG 的 OPO 激光性能。(a)中红外输出功率；(b)激光输出功率为 107 W 时的光束质量

Fig. 3　OPO laser properties of ZPG. (a) Mid-IR output power; (b) beam quality at laser output power of 107 W

采用超低梯度冷凝技术结合晶体后处理工艺，可以获得大口径超低吸收系数中红外 ZGP OPO 器件。研究结果有利于构建紧凑、高效的高功率大能量中红外光源。除材料因素外，器件表面和膜层也是薄弱环节，表面的光滑程度和增透膜的质量都影响器件最终的损伤阈值，这将是下一步工作的重要研究内容。

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Fabrication of Mid-Infrared $ZnGeP_2$ Crystals and Devices with Large Apertures and Ultra-Low Absorption Coefficients

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Abstract

Objective　Nowadays, the optical parametric oscillator (OPO) technique through mid-infrared nonlinear optical (NLO) crystals is an important way to generate tunable high power all-solid-state 3–5 μm mid-infrared laser sources which have many important civil and military applications including atmospheric monitoring, medical diagnosis, and photoelectric countermeasures. In OPOs, the infrared nonlinear optical crystal is critical as its quality determines the output power of a mid-infrared laser. Zinc germanium phosphide, ZnGeP$_2$ (ZGP), possesses a high nonlinear coefficient, a high damage threshold, and good thermal conductivity and is transparent and phase matchable at 2 μm, and thus it is called "the king of mid-infrared nonlinear optical crystals". However, there is an abnormal optical absorption band in the wavelength region of 0.7–2.2 μm that hinders the output power increase of ZGP OPOs. In order to meet the demands of applications that require higher efficiencies and output powers, absorption losses at the abnormal optical absorption band have to be further reduced.

Methods A highly-pure polycrystalline ZGP is synthesized by using a self-made two-zone tube furnace. Large ZGP single crystals are grown by the gradient freezing method. ZGP OPO devices are fabricated after orienting, cutting, post-growth thermal annealing, polishing, and coating. A spectrophotometer is used to measure the spectrum of ZGP. The OPO laser experiment is carried out with one ZGP device pumped by a 2.09 μm Ho:YAG pulsed laser with a pulse repetition rate of 20 kHz.

Results and Discussions In this study, high quality large ZGP single crystals with diameters of 3.8–5.0 cm have been successfully grown by the freezing method with an ultralow gradient (0.5–1 ℃/cm) in the self-made furnaces with growth yields over 95%. Figs. 1 (a) and (b) show the ZGP crystals grown by HGF and VGF, respectively. The ZGP OPO crystal devices with various specifications [Figs .1 (c) and (d)] are fabricated with the maximum size up to 30 mm × 30 mm × 40 mm (the largest ZGP OPO device fabricated to date) after orienting, cutting, post-growth thermal annealing, polishing, and coating. The absorption coefficients of ZGP devices prepared by the normal electron-beam irradiation (Ⅰ) and the freezing method with ultralow gradient (Ⅱ) are measured and compared, as shown in Fig. 2. The absorption coefficients for Ⅰ are 1.8 cm^{-1} and 0.04 cm^{-1} at 1.064 μm and 2.09 μm, respectively. As a comparison, the absorption coefficients for Ⅱ are much lower with values of 0.4 cm^{-1} and 0.015 cm^{-1}, respectively. The ultralow absorption coefficients promote the improvement of conversion efficiency and the increase of output power of ZGP OPOs. The OPO laser experiments are carried out with a 6 mm × 6 mm × 30 mm ZGP device pumped by a 2.09 μm Ho:YAG pulsed laser with a pulse repetition rate of 20 kHz. A maximum average output power of 107 W at 3–5 μm is obtained with a 173 W incident pump power, corresponding to a slope efficiency of 75% and an optical-optical efficiency of 61.8%, as shown in Fig. 3(a). The beam quality factors (M^2) are 3.13 and 3.14 for horizontal and vertical directions [Fig. 3(b)], respectively.

Conclusions In this study, high quality ZGP crystals with diameters of 3.8–5.0 cm have been grown by the ultralow gradient freezing technique in self-made furnaces with growth yields over 95%. The crystal growth efforts and post processing have resulted in ZGP OPO devices with an ultra-low absorption loss (0.015 cm^{-1}@2.09 μm) and a size of up to 30 mm × 30 mm × 40 mm. A high average output power (>100 W) ZGP OPO with only one low absorption ZGP device has been demonstrated, with no obvious limits to further scaling. The results indicate that the combination of large aperture and low absorption losses makes our ZGP crystals extremely attractive for high average power and high energy applications.

Key words laser technique; mid-infrared nonlinear optical crystal; ZnGeP$_2$ single crystal; ultralow gradient freezing method; high power mid-infrared laser