Improvement of $ZnGeP_2$ optical quality by investigating growth conditions and high energy electron irradiation

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$ZnGeP_2$ (ZGP) is a promising crystal for frequency conversion in the mid-IR, thanks to a high non-linearity coefficient, a wide transparency band from 0.74 to 12 µm, as well as an important thermal conductivity for high power applications. These excellent properties allow ZGP to be implemented in Optical Parametric Oscillator (OPO) devices to produce powerful and tunable laser beams in the 3-12µm range from a 2µm pump. These sources are major for various applications such as long-range detection of gases, active imaging, or surgery [1].

However, the processing of high optical quality ZGP is complex. It has a relatively high melting point (1029°C) and contains volatile and toxic compounds, like phosphorus, which has a high vapor pressure above 500°C, requiring encapsulation in an evacuated quartz ampule. To limit the pressure, and so the rupture of the reactor, a two-zone temperature synthesis is used [2]. After the compound synthesis, a crystal growth step is carried out in a vertical Bridgman furnace, where the melt of the previously synthetized material is pulled from a single-crystal seed. Excesses of Zn and P are introduced in the preparation to minimize deviation from stoichiometry resulting from the compounds volatility. We will present experimental attempts to improve the processing of ZGP crystal growth.

Furthermore, in as-grown crystals, the optical quality of ZGP is affected by the presence of point defects, mainly the paramagnetic zinc vacancy: V_{Zn}^- [3]. They create an absorption band, which impinges the OPO pumping wavelength at 2 µm. Researches have shown that post-growth annealing near 600°C [4], and electron irradiation [5], reduce this absorption by decreasing the concentration of paramagnetic defects. These defects are characterized at the LSI using EPR (Electron Paramagnetic Resonance). We will present EPR data recorded on electron irradiated $ZnGeP_2$ single crystals, focusing on the effect of irradiation temperature and irradiation fluence on the V_{Zn}^- defect concentration. First, our data suggests that irradiation is more efficient at 20°C to reduce the V_{Zn}^- concentration. Then, our data shows that irradiation allows reducing up to five times the V_{Zn}^- concentration with a fluence of 2.10^{17} e/cm².

In the future, we would like to carry out optical transmission measurements during the irradiation to further understand the influence of irradiation on the defects, as well as investigate a doped crystal $ZnGeP_2$:Sn, to improve optical quality for OPO achievement purpose.

References

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