Growth, defect characterizations and applications of α-GeO_2 bulk crystals

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The Top Seeded Solution Growth – Slow cooling (TSSG-SC) technique allowed us to grow centimeter size single crystals of α-GeO_2 by using the chemical system GeO_2 - $K_2Mo_4O_{13}$ – $K_6P_4O_{13}$. These crystals do not show any phase transition before the melting temperature (≈ 1000 °C) and only a small evolution of the piezoelectric constants and dielectric properties up to 600 °C [1], contrary to α-GeO_2 crystals when grown hydrothermally [2]. That makes our α-GeO_2 crystals potential good candidates to be used in harsh conditions and high temperature environments.

However, α-GeO_2 crystals grown by TSSG-SC show optical twins. Their characterization has been done in several slabs of different orientations ([010], [001], [110] and [101]) by using three complementary techniques: visualization through crossed polarizers, X-ray topography and chemical etching. By crosschecking all the experimental data, we determined the orientation of the walls that separate different twinned zones and we established that these defects do not originate close to the seed in the very early stage of crystal growth.

α-GeO_2 crystallizing in the chiral space group $P3_121$ (or $P3_221$), it is non-centrosymmetric crystal, which allows nonlinear frequency conversion from second-order processes. We recently performed, for the first time to our knowledge, such studies by using a 9-mm-diameter cylinder shaped in a α-GeO_2 crystal combined with tunable pulsed beams. We recorded phase-matching curves of Second Harmonic Generation (SHG). We also studied Sum- and Difference- Frequency Generations (SFG and DFG). From the analysis of all the experimental data, we reported reliable Sellmeier equations describing the variation of the principal refractive indices of this uniaxial crystal as a function of wavelength. With these dispersion equations, our calculations showed that α-GeO_2 crystals can generate a super continuum tunable between 1.2 µm and 3 µm when pumped at 0.86 µm and oriented at 48.3° from [001]. The magnitude of the nonlinear coefficient d_{11} of α-GeO_2 was also determined relatively to KTP [3].

Surface acoustic wave properties of α-GeO_2 have been also investigated numerically [4]. It led us to propose this crystal as a substrate for designing and realizing a passive transducer compatible with short range RADAR interrogation [5].

All these results provide a proof of the real potentiality of α-GeO_2 crystals grown by TSSG-SC despite optical twins. We plan further *in situ* studies in order to determine the origin of the twins, to understand the way they evolve during the crystal growth, and finally find the growth conditions needed to obtain twin free single α-GeO_2 crystals.

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