HT CrystalSolutions LLC

Summary of NSF SBIR proposal submitted June 2017 on SBBO a novel deep UV NLO,

We are proposing the development of a new phase of a strontium beryllium borate, $Sr_2Be_2B_2O_7$ (SBBO), a nonlinear optical crystal we discovered using a novel hydrothermal crystal growth process. The new polymorph has a very high nonlinear conversion, a suitable birefringence, a wide bandgap, very high optical damage threshold, stability to water and most importantly, is hard and physically robust. This latter quality makes the material capable of being cut, polished and coated for use in laser cavities. Another polymorph of this crystal was originally reported by other workers but grown by a flux melt method that inevitably introduced severe disorder in the crystal. The acute disorder of the borate groups in the earlier material introduces major ambiguities in the structure and cancels out much of the nonlinear effects, effectively negating all of the positive properties of the material. Our new hydrothermally grown crystals are well ordered and contain no ambiguities in the unit cell or in the arrangement of the borate groups. Thus our new version of SBBO contains all of the positive attributes of the material while eliminating the one serious limitation, making it a potentially disruptive technology for the manufacture of solid -state deep-UV lasers.

The development of our new crystal for commercial production will allow for the construction of lasers operating in the deep-UV, between 300 and 200 nm, with all solid-state construction. They will be rugged, compact, reliable and long lasting. By being field deployable they will allow access to many new markets including laser surgery, micromachining, standoff detection of hazardous materials and many others. The new crystal can be straightforwardly inserted into existing solid-state laser pumps to generate efficient new deep-UV lasers. The benefits for any laser company in this area would be a compact, reliable efficient UV laser system. Once the protocol for crystal growth is developed the cost and reproducibility of the NLO crystal will be very favorable.

The customers will be any laser manufacturer interested in producing UV/deep-UV (≤266nm) solid-state lasers. There are currently a number of markets with unmet demand for deep-UV solid-state lasers, including microlaser surgery, chem/bio standoff detection, spectroscopy, micromachining and imaging of microelectronics. Current technology is limited to gas lasers, which are large, bulky and difficult to deploy in the field. The primary bottleneck to all-solid-state lasers at this point is lack of efficient nonlinear optical crystals capable of frequency shifting powerful visible laser wavelengths to the short wavelength UV. Existing crystals are limited by low conversion efficiency, hygroscopic instability, insufficient bandgap, low birefringence or poor processibility.

Our new polymorph of SBBO grown using our novel hydrothermal method crystallizes in a different space group (P6(-)) and new, *completely unambiguous unit cell* (a = 4.6709 c = 3.841). [1] The critical difference between our SBBO and the previously reported material is that ours contains fully ordered borate groups. (Figs. 1, 2) The unit cell is much more compact than the previously reported one, with a c axis one fourth of the disordered material. This dramatically increases the NLO performance of the material. Even more importantly the precise and accurate determination of the new unit cell will enable accurate determination of Sellmeier coefficients, refractive index values and phase matching angles. Our preliminary evaluation of the new polymorph of SBBO using a standard Kurtz experiment indicates that its NLO conversion efficiency of 864 to 432 nm wavelength is nearly four times higher than that of industry standard BBO in that region. Since the *original* disordered polymorph of SBBO was originally reported to have an NLO d_{eff} approximately comparable to BBO (ca. 2.2 pm/v), this strongly suggests that the *new* polymorph of SBBO will be several times more efficient in NLO behavior than the current industry-best material, be more chemically stable than BBO and be capable of performance at much shorter wavelength than any existing commercial single crystals (≤200nm).

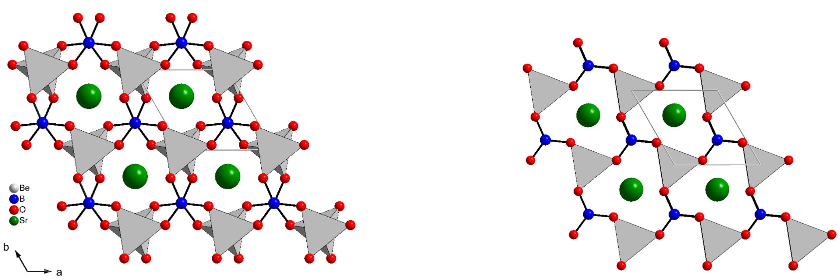

Figure 1. Top view of disordered SBBO structure showing rotated borate groups (left) and new polymorph of ordered SBBO highlighting perfectly aligned borate groups

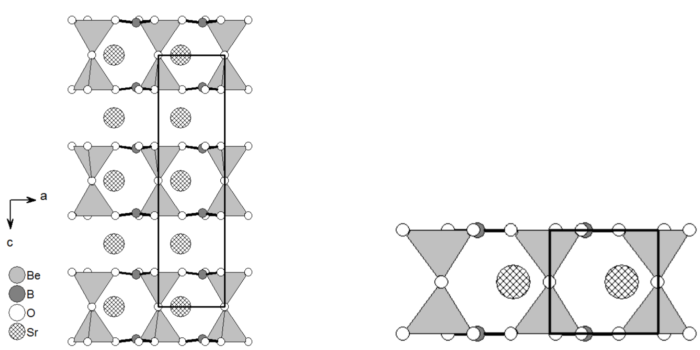

Figure 2. Side view of disordered SBBO structure showing elongated disordered unit cell (left) and new polymorph of ordered SBBO highlighting compact ordered unit cell.

The original authors reported that they could never obtain a decent R factor (>0.065) or satisfactory refinement on their disordered crystals with unstable oxygen atom locations.[2]

Our refinement on our ordered crystals is excellent with an R factor of 0.015 with stable refinement on all atoms. Furthermore omega scans of several diffraction peaks display narrow, highly symmetrically shaped peaks indicating high quality crystals with no disorder. This new SBBO polymorph contains all of the positive attributes of the previous SBBO crystals (short wavelength band edges, hard surfaces, high optical damages threshold, good birefringence and good NLO behavior) with the improvements described above (no disorder, small dense unit cells, very high NLO coefficients excellent crystal quality).

1. J.W. Kolis, C.D. McMillen "Hexagonal Beryllium Borate Crystal" USPTO patent submitted.
2. C. Chen, Z. Lin, Z. Wang "The Development of New Borate-Based UV Nonlinear Optical Crystals" Appl. Phys. B **2005**, B80 1-25.