ABSTRACT

Lasers find a vast number of applications such as: fiber optic communication, micromarking and microsurgery, industrial drilling and welding, remote sensing and range-finding, to just mention a few. Ultraviolet (UV) radiation is reviewed as a clean source for materials synthesis and processing. Excimer lasers are the useful source of intense UV radiation. Operation of these lasers involved high-voltage discharge of corrosive gas. A compact maintenance free all-solid state alternative is in high demand and its characteristic features are advantageous in both research and industrial applications. Examples of these are high efficiency, good beam quality and the possibility of Q-switching. A serious limitation of a conventional solid-state laser is that it cannot have an arbitrary wavelength. Nonlinear optics provides a solution to this problem, by the use of parametric processes in nonlinear materials. Thus, radiation of other frequencies than those produced directly by lasers can be obtained. NLO crystals that generate visible and UV lights effectively are important for the realization of a high-power, all-solid-state UV light source.

Until 1975, most NLO crystals were based on the P-O, I-O and Nb-O bonds like those in KDP (KH₂PO₄), LiIO₃, KNbO₃ and LiNbO₃. The KTP (KTiOPO₄) crystals developed later provide properties that merely combined those of KDP and LiNbO₃. This makes KTP potential for both high power and semiconductor laser operations. Because of the large number and diversity of present and projected applications, no single NLO material can be optimized for all uses. Thus far only a limited number of efficient NLO materials have been commercialized, thereby creating a bottleneck in the use
of lasers in the advancement of many key technology areas. As a result, there is a continuing search for and development of new NLO materials.

The relatively high resistance against laser-induced damage and higher transparency in the UV region are the reasons for NLO crystals with B-O bonds to be often employed for high-power UV light generation. The optical properties of borate crystals appeared to be related to their molecular structure. Intense research led to the development of borate crystals like KB₅O₆·4H₂O (KB5), β-BaB₂O₄ (BBO), LiB₃O₅ (LBO), CSLiB₂O₁₀ (CLBO), YCa₄O(BO₃)₃ (YCOB), CsB₃O₅ (CBO), GdₓY₁₋ₓCa₄O(BO₃)₃ (GdYCOB), K₂Al₃B₂O₇ (KAB), KBe₂BO₃F₂ (KBBF), Sr₂Be₂BO₇ (SBBO). These crystals are constructed from three basic structure units: (B₃O₆)³⁻, (B₂O₇)⁵⁻ and (BO₃)³⁻ anionic groups. The UV absorption edge of crystals containing the (B₃O₆)³⁻ group occurred at a longer wavelength (e.g. BBO) as compared to those constructed from the (B₂O₇)⁵⁻ group (LBO, CBO and CLBO). Both CBO and LBO are constructed from a continuous network of nonplanar (B₂O₇)⁵⁻ groups with interstitial Cs and Li cations, respectively. Based on the absorption edge, (B₂O₇)⁵⁻ group is ideal as the basic structural unit of deep UV NLO materials.

Cesium triborate, CsB₃O₅ (CBO) was predicted as a useful borate NLO crystal by Chen et al in 1989. CBO is transparent up to the UV region and has a large effective nonlinear optical coefficient. In the present investigation, CBO crystals have been grown by TSSG technique using a five-zone resistive heated furnace. CBO charge is highly volatile because of the cesium component leading to unstable growth and spontaneous nucleations. The spontaneous nucleations are also influenced by the change of saturation temperature induced by heavy evaporation. The cesium-rich volatiles posed a problem by attacking the seed crystal and caused the dissolution of the seed.
During growth the seed crystal was covered with a platinum foil and the seed crystal was little dipped into the solution so that no part of the seed except that covered with the platinum foil was exposed to the harmful volatiles. By TSSG growth technique, large CBO crystal of size $50 \times 45 \times 45 \text{ mm}^3 (a \times b \times c)$ and weighing about 159.2 g has been grown and its structure has been confirmed by powder X-ray diffraction studies.

Scattering centers were observed in crystals grown from 74 mol% B$_2$O$_3$ solutions when illuminated with a 4 mW He-Ne laser. Weight loss of 20 mg powdered crystals grown from 74 mol% B$_2$O$_3$ solutions was measured at different temperatures in air using thermo-gravimetry. The weight loss experiments revealed that cesium evaporation occurs during the growth of the CBO crystals making the crystal off-stoichiometric. During the slow cooling of the crystals, additional phase precipitation occurring near the critical 650 °C region could be the reason for the scattering centers in CBO crystals. We propose that CBO has a retrograde solid solution curve and the scattering centers are formed as a result of the off-stoichiometry. Although the scattering centers have been reduced by post-growth quenching of the crystals, it produced a green luminescence when illuminated with a deep UV laser. The green luminescence is caused by the cesium vacancies that are created by the dissolution of scatters in the solid solution at high temperatures. To remove the scattering and green luminescence, the off-stoichiometric as-grown crystals were brought to the stoichiometric composition by the Vapour Transport Equilibration (VTE) process in the presence of cesium-rich solution. By our hypothesis of retrograde solid solution curve, we are able to explain the mechanism of scattering centers and green luminescence formation in CBO crystals.
The scattering centers are responsible for the optical loss and reduction in the third harmonic efficiency and the damage threshold. Though VTE and quenching experiments were successful in reducing the scattering centers, the laser induced damage thresholds of these crystals were lower than as-grown crystals. So an alternative approach was adopted and after growth the crystals were fast-cooled from about 830 to 500 °C. Different crystals were grown by changing the fast cooling in 1h, 3h and 6h to shorten the time exposed in the state of the high temperature. The fast-cooling process decreased the scattering centers and thereby increasing the bulk LIDT.

CBO has a deliquescence property and the surface of the crystals gets degraded by moisture absorbed from the atmosphere. The FTIR spectrum taken after exposing the crystal to the moisture content in the atmosphere showed an absorption peak at 3400 cm\(^{-1}\). To reduce the surface degradation, the polished crystals were transferred to a stainless steel chamber purged with Ar gas. For practical applications, we optimised the conditions for maintaining the degradation free surface after laser irradiation. The processed ‘a’ axis crystals were irradiated with a third harmonic (355 nm) of the Nd:YAG laser at 300 mJ. The frequency of the laser was 10 Hz with a pulse width of 7 ns. After this processing, degradation on the crystals surface was considerably reduced. We have maintained the surface of the CBO crystal for laser applications and this process can be applied to other NLO crystals. The second harmonic (SHG) and third harmonic generation (THG) studies of CBO crystals have been studied. The CBO crystals were cut for type II generation and the SHG was generated from 3, 6 and 12 mm crystals. The CBO crystal was cut for type II THG and a high power of 100 W and 150 W was generated.