CHAPTER 4

IMPROVEMENT OF LIDT AND REDUCTION OF SURFACE DEGRADATION IN CBO CRYSTALS

4.1 IMPORTANCE OF LASER DAMAGE AND COMPARISON WITH OTHER CRYSTALS

It is well known that NLO materials are generally used for optical modulation, Q-switching, and frequency multiplication in high-power laser systems (Eaton 1991). For harmonic generation, the conversion efficiency is strongly dependent on the incident power level. The operation of nonlinear optical devices obviously involves the exposure of these materials to high intensity laser light. Hence, the utility of NLO crystal depends not only on the linear and nonlinear optical properties but also largely on its ability to withstand high power lasers (Glass and Guenther 1973). Laser damage studies on NLO crystals are extremely important as the surface damage of the crystal by high power lasers limits its performance in NLO applications (Boling et al 1973). The knowledge of damage threshold is essential as NLO crystals are generally used for long durations as per the demands of various applications in research and industry.

Among NLO crystals the borate family possess a high level of damage threshold. The bulk laser damage of borate crystals like LBO, BBO and CLBO have been reported. (Eimerl et al 1987, Nakatani et al 1988, Furukawa et al 1994, Yoshimura et al 1999b). There are reports on the laser induced damage tolerance measurements on KDP and KTP in the SPIE

In this investigation, the laser-induced damage threshold of CBO crystal was measured by using 1-on-1 method. The laser damage mechanism in 1-on-1 method is described here.

4.2 MECHANISM OF LASER-INDUCED DAMAGE

The first chance that the optical medium's damage happens is a photo-absorption of the material. It transmits in the material and the photon energy is transmitted to the electron in the orbit of the atom. As a result, the energy of the electron changes from lower (ground state) to higher energy state. When the energy of excitation is small, it returns to the ground state by the energy diffusion (lattice easing) by the local photon transformation generated in the circumference of the electron. However, ionizing is caused when energy is high enough so that the photon energy may discharge the electron (free electron) from the atom (photo-ionization). The avalanche-breakdown mechanism is believed to be the dominant damage mechanism for most pulsed lasers.

The nature of the mechanism is that a small number of free electrons are accelerated to high energies through the interaction with the laser field. These electrons can then impact-ionize other atoms within the materials, thereby producing additional electrons which are subsequently
accelerated by the laser field and which eventually produce still more electrons. Some fraction of the energy imparted to each electron will lead to a localized heating of the material, which can eventually lead to damage of the material due to cracking or melting. The few electrons initially present within the material are created by one of several processes, including thermal excitation, quantum mechanical tunneling, free electrons resulting from crystal defects.

Laser-induced bulk damage may occur due to many intrinsic and extrinsic factors. Intrinsic damage that limits the optical strength of materials includes linear absorption, some nonlinear effects such as self-focusing, multiphoton absorption, stimulated Brillouin scattering, stimulated Raman scattering, and electron avalanche breakdown. On the other hand, extrinsic damage includes material defects, impurities and finished surface of materials. Many studies have focussed on different laser parameters such as pulse duration, beam spot size, transverse and longitudinal laser modes, and laser wavelength. However it is difficult to extract comparable information from previous reports. The damage threshold of nonlinear crystals changes with sample type of various compositions and with localized imperfections, and absorption centers (Yoshida et al 2006).

4.3 SETUP FOR THE BULK LASER INDUCED DAMAGE THRESHOLD BY THE 1-ON-1 METHOD

As the CBO crystal is mostly used for THG of the Nd:YAG laser, it is very important to evaluate the damage tolerance at this wavelength as this would be practical for many industrial applications. There is no report on the bulk LIDT data of the CBO crystals in the ultraviolet region. The damage threshold has been evaluated using an 1-on-1 technique by the third-harmonic (355-nm) light of longitudinal single-mode Q-switch Nd:YAG laser (Continuum, Powerlite Plus). We measured the damage tolerance of CBO and
fused quartz (Shin-Etsu, OX) with the same experimental setup. By using reference data for fused quartz, the absolute damage tolerance value of CBO was estimated. Similar reports on the damage threshold of CLBO based on fused quartz have been reported (Mori et al 2002, Kamimura et al 2001).

The bulk damage threshold of CBO crystal was determined by the 1-on-1 technique. This is a method of doing the damage evaluation by judging the presence of the bulk damage, and the crystal was moved 1 mm each time when a new laser pulse was irradiated. The third harmonic of Q switch Nd:YAG laser in horizontal single mode was used for the measurement as shown in Figure 4.1. The pulse width is about 6 ns, and the laser energy of about 80–750 μJ falls on the sample through a lens of focal length 100 mm.

Figure 4.1  The setup for the laser induced damage tolerance by using the third harmonic of the Nd:YAG laser
The position of the crystal was adjusted so that the laser beam was focused to a point 5-mm inside the crystal from the entrance surface. The purpose of this focusing was to make sure that the occurrence of the laser damage on the surface would not influence the evaluation of the bulk damage tolerance in the crystal. Prior to every single shot, the irradiation site was checked with a He-Ne laser to ensure that there were no newly created scatters at the focal point. Then the single pulse of the 355 nm laser was irradiated till the damage occurs in the crystal.

Damage was considered to have occurred when the scatters appeared are newly generated after the shot on the same axis as the 355 nm laser through the He-Ne laser. When incidence energy is higher than the damage threshold, generation of plasma causes the damage to occur. The generation of the damage was identified by the scattering formed by the He-Ne light and it is only formed in the vicinity of the threshold. The strength of the laser pulse was adjusted by combining $\lambda/2$ board ($\lambda$=355 nm) (polarized light rotator) and the polarizer. The laser beam was incident normal to the (011) face of an optically polished CBO crystal and was polarized along the $a$-axis.

4.4 MEASUREMENT OF BULK LIDT IN CBO

The position was moved by 1 mm for every one shot and the laser light of $a$-axis polarized light was irradiated, and measured. By using reference data for fused quartz, the absolute damage tolerance value of CBO was estimated. The absolute value was calculated based on the value of fused quartz which has been reported in the past (Yoshimura et al 1999b). The damage threshold of fused quartz is reported to be about 13 GW/cm$^2$ by Kuzuu et al (1999) for light of 355 nm wavelength and pulse width of 0.85 ns. The damage threshold of CBO crystal was found to be 2 times that of fused
quartz. The pulse width of the 355-nm light was 6 ns, and the bulk LIDT of the CBO crystal by using the $\sqrt{\tau}$ scaling rule (Koechner 1999) was estimated to be about 11 GW/cm$^2$ for 355 nm.

4.4.1 Damage Tolerance of VTE and Quenched Crystals

The scattering centers are responsible for the optical loss and reduction in the third harmonic efficiency and the damage threshold. To reduce the scattering centers the quenching and the VTE experiments were carried out. Though these experiments were successful in reducing the scattering centers, there were some defects induced in these crystals as a result of reheating to high temperatures. This was confirmed by the laser induced damage threshold of these crystals. The damage threshold of the VTE and quenched crystals were lower than that of the as-grown crystals. For high power THG applications it is necessary that the crystals have high damage threshold. So these techniques were not effective for improving the quality of the CBO crystals. To increase the damage threshold of these crystals for high power industrial applications it was necessary to reduce the scattering center formation without the creation of new defects caused by reheating the crystals. So an alternative approach was adopted and this chapter explains about the technique for the reduction of scattering centers and simultaneous increase in the damage threshold of CBO crystals.

The experiments carried out by changing the starting temperature of quenching showed that the formation of scattering centers occurs during the cooling process at 650 °C. So it was necessary to surpass the dangerous 650°C. As post growth heating the crystals led to new defect creation we tried to reduce the scattering centers by fast cooling immediately after growth for surpassing the 650 °C region.
4.5 GROWTH OF CBO CRYSTALS BY FAST COOLING

The crystal growth of CBO from 74 mol% B$_2$O$_3$ solution was carried out at about 830 °C as described in Chapter 2. During the normal growth of CBO crystals, the crystals were cooled at a rate of 17 °C/h to room temperature after growth. From the retrograde solid solution of CBO we understand that during the slow cooling process, the scattering centers are precipitated at 650 °C regions. Immediately after the crystal attains the required size, it was pulled from the solution.

In the fast cooling process after pulling the crystals from the solution, the cooling rate was increased drastically. Figure 4.2 shows the different cooling programs that were adopted during the growth. The crystals were cooled quickly from 830 to 500 °C. Different crystals were grown by changing the fast cooling in 1 h, 3 h and 6 h (The cooling rate: 330 °C/h, 110 °C/h and 55 °C/h respectively) to shorten the time exposed in the state of the high temperature. Then slow cooling was done from 500 °C up to room temperature at a cooling rate of 17°C/h as shown in Figure 4.2.

It was difficult to reduce the cooling rate of the furnace from 833 to 500 °C for the fast cooling rates. So after pulling the crystals from the furnace, a thermocouple was inserted at the position of the grown crystal. Care was taken to control the temperature of the furnace, in such a way that it follows the appropriate cooling program. However, cracking was observed in the crystal grown at a fast cooling rate of 330 °C/h.
4.6 INTENSITY OF SCATTERING FOR FAST COOLED CRYSTALS

The crystals grown by different cooling programs are shown in the Table 4.1. The change in the intensity of the scattering centers for the crystals was observed by irradiating with a He-Ne laser (633 nm). The incident beam direction was normal to the (100) crystal face, and the polarization was parallel to the <100> direction. The direction of observation of the scattered light was from the other (011) face perpendicular to the beam direction.
From the Table 4.1 it can be clearly seen that the intensity of scattering centers were less for crystals grown at a cooling rate of 330 °C/h. The scattering centers decreased as the cooling rate of the grown crystals was increased. The grown crystals were also compared with the as-grown crystals (grown by the conventional cooling rate from 74 mol% B₂O₃ solutions) which had the highest intensity of scattering centers. This experiment further confirmed that because of the retrograde solid solution curve of CBO, when the dangerous 650 °C was surpassed the scattering centers could be avoided.

4.7 LIDT MEASUREMENTS FOR THE FAST COOLED CRYSTALS

The bulk LIDT of fast cooled crystals was determined by the 1-on-1 technique using the same setup as described previously in this chapter. The laser beam was incident normal to the (011) face of an optically polished CBO crystal and was polarized along the \( a \)-axis. By using the reference data for fused quartz, the absolute damage tolerance value of CBO was estimated. The pulse width of the 355-nm light was 6 ns, and the bulk LIDT of the CBO crystal was estimated by using the \( \sqrt{r} \) scaling rule. The result of the bulk LIDT for the fast cooled crystals with reference to fused quartz is presented in Figure 4.3.

It can be clearly seen from Figure 4.4 that bulk LIDT of the crystals increases with the increasing cooling rate. The bulk LIDT was highest for the fastest cooled crystals (330 °C/h) and was 3.7 times that of fused quartz. In comparison to the crystal grown by conventional cooling technique (17 °C/h) the LIDT has increased by 85%. The scattering centers in the crystals have also been reduced. The results confirm that long time exposure at high temperature has an adverse effect on the CBO crystal. The optical quality and the bulk LIDT of the CBO crystals has been increased by fast cooling process.
Table 4.1 The crystals grown by the cooling rate of 330 °C/h, 110 °C/h and 55 °C/h and 17 °C/h from 833 to 500 °C

<table>
<thead>
<tr>
<th>Cooling rate</th>
<th>17°C/h</th>
<th>55°C/h</th>
<th>110°C/h</th>
<th>330°C/h</th>
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<tr>
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</tbody>
</table>
Figure 4.3  Cut and polished fast-cooled crystals used for the LIDT measurements

Figure 4.4  Bulk LIDT of fast cooled crystals with respect to the cooling rate
4.8 REDUCTION OF SURFACE DEGRADATION OF THE CBO CRYSTALS

Frequency conversion of high-power solid-state laser light in NLO crystals is an attractive method for producing UV radiation from compact, efficient, and reliable systems. The performance of such solid-state UV lasers depends greatly on the properties of the NLO crystals. CBO has a deliquescence property and the surface of the crystals gets degraded when exposed to moisture content in the atmosphere. The surface degradation gets further increased during laser irradiation as shown in Figure 4.5. Even when the pulse energy was two or three orders of magnitude less than the damage threshold, gradual degradation of the THG power would occur if the surface degradation was not controlled. Surface hydration in air occurs with many crystals, such as KDP, LBO, or even CLBO (which is more hygroscopic). Therefore, more information is needed to relate the surface degradation mechanism to hydration.

Figure 4.5 Surface degradation of CBO crystal after laser irradiation
The mechanism of the degradation seemed not to be established, and was believed to be due to optical and mechanical stresses introduced by crystal hydration or the accumulation of the surface laser damage by the impact of high-energy UV laser light. A new mechanism for the reduction of surface damage in CBO crystals is proposed. We tried to investigate the relationship between the surface damage and effect of water vapour. Dependence of the hydration rate with time have been investigated by FTIR and summarized that hydration seemed to cause surface degradation. The problems of surface degradation have been reduced by treating the crystal in the presence of Ar gas flow. This process could also be applied to other NLO borate crystals which have a hygroscopic property and hence the degradation on the surface of the crystals could be reduced.

In order to prevent the cracking, it is necessary to understand the cracking mechanism. Similar surface degradation was observed when the crystal was repeatedly heated and cooled from 50 °C to room temperature. We suppose the same phenomenon of subsequent heating and cooling occurred on the crystal surface during laser irradiation. During the cooling periods there is a greater chance for the absorption of water and further irradiation of laser causes the degradation to occur. To check the absorption of water by the surface of the crystal, Fourier transform infrared (FTIR) spectroscopy was performed. The absorption bands due to the OH group arise near 3500 cm\(^{-1}\) for LiNbO\(_3\), KTP and CLBO crystals (Herrington et al 1973, Zumsteg et al 1976, Nishioka et al 2005). The FTIR spectrum was measured in the transmission mode in the wavenumber region 2500 to 6000 cm\(^{-1}\). For the measurements the incident IR beam was directed normal to the crystal surface. The FTIR spectrum taken after exposing the crystal to the moisture content in the atmosphere showed an absorption peak at 3400 cm\(^{-1}\).
However the FTIR spectrum taken immediately after polishing the surface of CBO crystal showed no absorption peak near 3400 cm\(^{-1}\). It has been reported that cesium diffuses to the outer surface of CBO and the surface is covered by a cesium-rich amorphous layer. This suggests the cesium-rich CBO surface has absorbed the water vapour from the atmosphere and produced the absorption peak. To establish a method for tentatively determining the absorption of the moisture by the crystal’s surface, the FTIR spectra of the sample exposed to the humid atmosphere for various time periods were measured. In Figure 4.6 the graphs a, b, c, d, e and f represents the gradual appearance of the absorption peak in the FTIR spectrum for different exposure time periods of 5min, 1h, 2.5h, 4h, 5h and 1day respectively. The interaction of the laser irradiation on the hygroscopic cesium-rich surface enhanced the surface degradation.

The absence of the FTIR absorption peak (3400 cm\(^{-1}\)) taken immediately after polishing the crystal suggests that it is possible to reduce the degradation, if the crystals were concealed from the atmospheric water vapour. To reduce the surface degradation, the polished crystals were transferred to a stainless steel chamber purged with Ar gas. The chamber containing the crystal had calcium fluoride glass windows in one direction for the crystal to be irradiated by laser light as shown in the Figure 4.7.
Figure 4.6 The gradual appearance of the absorption peak at 3400 cm\(^{-1}\) when the crystal was kept in normal ambient

Figure 4.7 The chamber having calcium fluoride glass windows used for concealing the surface from the atmospheric moisture
The FTIR spectrum of the crystal inside the chamber was checked periodically. It was found that even after keeping the crystal inside the Ar filled chamber for a long time, the absorption peak at 3400 cm\(^{-1}\) did not appear. The conditions were optimised for maintaining the degradation free surface and surface was checked with an optical microscope. To remove the small amount of water vapour in the chamber the following steps were taken. The Ar flow (15 ml/min) inside the chamber was started 10 min before keeping the \(a\)-axis crystal inside the chamber. After keeping the crystal, the chamber was sealed and slowly heated to 150 °C. The crystal was annealed at this temperature for 12 h and then slowly cooled to room temperature. After this processing there was less degradation on the crystals surface when viewed with an optical microscope.

The surface of the crystal was also checked after irradiation with a laser. During these experiments the humidity content in the atmosphere was 35-50%. The crystals were irradiated with a third harmonic (355 nm) of the Nd:YAG laser. The frequency of the laser was 10 Hz and the pulse width was 7 ns. An optically polished crystal was irradiated for 1 h in air and the energy was adjusted till similar surface degradation was observed. For an input energy of 300 mJ, clear surface degradation was observed (Figure 4.8a). As the laser could be used for the surface studies, we carried out the experiment in the chamber filled with Ar gas.

The processed \(a\)-axis crystals were irradiated with the third harmonic beam at 300 mJ. After this processing there was less degradation on the crystals surface as shown in the Figure 4.8b. To check the effect of annealing, the same experiment was repeated in normal ambient (absence of Ar flow) at 150 °C. But degradation on the surface of the crystal was observed (Figure 4.9a). So the presence of Ar gas was important to reduce the surface degradation in CBO. The experiment was also carried out for \(c\)-axis
samples and the surface degradation was reduced after the processing conditions as shown in Figure 4.9b. We have maintained the surface of the CBO crystal for laser applications and this process can be applied to other NLO crystals.

Figure 4.8 The surface of the \( a \)-axis crystal (a) after irradiating with the 355 nm laser at 300 mJ in normal ambient and (b) after surface processing in Ar ambient and irradiating with a 355 nm laser at 300mJ
Figure 4.9  (a) The surface of the \( a \)-axis crystal after processing without Ar ambient and irradiating with a 355 nm laser at 300 mJ and (b) The surface of the \( c \)-axis crystal after surface processing in Ar ambient and irradiating with a 355 nm laser at 300 mJ.
4.9 CONCLUSIONS

The scattering centers are responsible for the optical loss and reduction in the third harmonic efficiency and the damage threshold. To reduce the scattering centers in CBO crystals the quenching and the VTE experiments were carried out. Though these 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 for 1 h, 3 h and 6 h (The cooling rate: 330 °C/h, 110 °C/h and 55 °C/h respectively) to shorten the time exposed in the state of the high temperature. The density of the scattering centers decreased whereas the bulk LIDT of the fast-cooled crystals increased as the cooling rate was increased.

CBO crystal has a deliquescence property and the surface of the crystals gets degraded when exposed to moisture content in 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 establish a method for tentatively determining the absorption of the moisture by the crystal’s surface, the FTIR spectra of the sample exposed to the humid atmosphere for various time periods were recorded. To reduce the surface degradation, the polished crystals were transferred to a stainless steel chamber purged with Ar gas.

The conditions for maintaining the degradation free surface were optimized after irradiation with a laser for practical application. The crystals were irradiated with a third harmonic (355 nm) of the Nd:YAG laser. The frequency of the laser was 10 Hz and the pulse width was 7 ns. The processed \(a\)-axis crystals were irradiated with the third harmonic beam at 300 mJ. After
this processing, there was less degradation on the crystals surface. We have maintained the surface of the CBO crystal for laser applications and this process can be applied to other NLO crystals.