UV light generation by $CsLiB_6O_{10}$ and effect of doping on crystal properties

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Abstract

We report on the fourth and fifth harmonics generations of Nd:YAG laser radiation realized in $CsLiB_6O_{10}$ (CLBO). The values of 500 mJ and 230 mJ at 266 nm and 213 nm were obtained from 2200 mJ of fundamental energy. Doping of CLBO has been carried out and the Al doping was found to give rise to an enhancement of mechanical and chemical properties.

Introduction

There has been an increasing interest in borate crystals for ultraviolet (UV) nonlinear optics (NLO) because all solid-state UV lasers obtained by NLO are strongly requested. Much effort has been spent on developing borates series, such as β-BaB_2O_4 (BBO)[1] and LiB_3O_5 (LBO),[2] in this decade. Recently another new borate crystal, $CsLiB_6O_{10}$ (CLBO), has been discovered and developed by the present authors.[3-6] In this talk, we report on the fourth and fifth harmonics generations of Nd:YAG laser radiation realized in CLBO. Effect of doping on various properties of CLBO are also discussed.

Harmonic generation of Nd:YAG laser

Table I shows values of angular, spectral and temperature bandwidths and walk-off angle for various frequency conversion process in the CLBO. For comparison, values of KDP and BBO calculated from the refractive index data are included. Despite the smaller nonlinear coefficient, CLBO possesses smaller walk-off angle, and larger angular and spectral bandwidths compared to BBO. The temperature acceptance of CLBO is larger that of BBO.

The Continuum Powerlite Plus Nd:YAG laser which can operate 10 Hz with pulse width of ~7ns was used to obtain 4HG and 5HG of Nd:YAG laser radiation in CLBO. The beam diameter was 12 mm. The transverse dimensions of CLBO crystal used were 12 x 12 mm^2 for 4HG and 5HG. The fundamental was doubled in a KD_2PO_4 (KD*P) crystal with type-II PM to obtain 532 nm radiation. The 10 mm long CLBO crystal was used for 4HG. Fifth harmonic generation was obtained in an uncoated 6 mm long CLBO crystal by type-I sum frequency generation (SFG) of the fourth harmonic and the fundamental. The fundamental and all harmonics beams propagated co-axially and they were physically separated from each other by a fused silica prism. Figure 1 shows various harmonic energies as a function of fundamental energy. We obtained output energy of 500 mJ at 266 nm with 50% 4HG efficiency from the second harmonic of 1000 mJ. The output pulse energies of 230 mJ at 213 nm was

Table 1. NLO properties of CLBO, KDP and BBO.

wavelength (nm)	Crystal	PM angle (θ)	calculated deff (pm/V)	Δθl (mrad-cm)	Δλl (nm-cm)	ΔTl (°C-cm)	Walk-off angle (deg)	Damage threshold (GW/cm²)
1064+1064 =532	CLBO (Type-II)	42.3	0.95	1.7	5.6	43.1	1.78	26
	KDP (Type-II)	59	0.38	3.4	11.5	19.1		~20
	BBO	22.8	2.06	0.92	2.1	37.1	3.20	13.5
1064+532= 355	CLBO (Type-II)	48.5	0.94	0.82	0.84	21.3	2.10	
	KDP (Type-II)	58	0.38	1.06	0.95			
532+532= 266	CLBO	61.6	0.84	0.49	0.13	8.3	1.83	
	KDP	78	0.51	1.7	0.13	1.2		
	BBO	47.5	1.32	0.17	0.07	4.5	4.80	
1064+266= 213	CLBO	67.3	0.87	0.42	0.16	5.1	1.69	
	BBO	51.1	1.26	0.11	0.08	3.1	5.34	

obtained for 6 mm sample from fundamental energy of 2200 mJ. This was corresponding to above 10% conversion efficiency of initial fundamental input energy. The harmonics output energy showed high stability for time interval more than 2 hours. We must also consider a loss of fundamental input energy for type-I SFG, because the mixing waves do not have the same polarization (fundamental wave is randomly elliptical polarized) in this experiment. Therefore, the use of the same polarization waves, resulting from type-I SHG of fundamental beam, would lead to a higher 5HG efficiency.

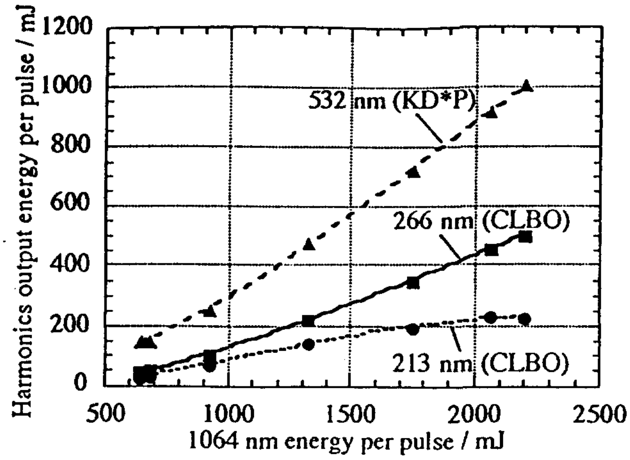

Figure 1. Harmonics output energies as a function of 1064 nm input energy.

Doping of CLBO

Doping impurities would affect the various properties of material. For borate crystals, such as BBO and LBO, systematic investigation has not been reported on doping so far. Recently we found that various metals can be used to dope CLBO. The four-circle X-ray diffraction (XRD) analysis revealed that impurities can be introduced to Cs site. The doping efficiency of these atoms, which is defined by the ratio of dopant concentration in the crystal with that in the melt (M/Cs; M = impurity), strongly depended on the element as shown in Figure 2. For alkali metals, the highest efficiency was observed for the Rb case and then for the K case. This can be explained that Rb^+ cation has the closest radii to Cs^+ cation compared with K^+ and Na^+ cations. The doping efficiency of Rb atom increases as increasing of the dopant concentration in the melt and almost 100% for the higher doping concentration. In contrast, an opposite tendency is seen for the K and Na cases. Much lower doping efficiency was observed for alkali earth metals compared to that of alkali metals. This may be due to the difference in the oxidation numbers between alkali and alkali earth metals. It is interesting that Al and Ga can be used to dope CLBO. Although they are group III element, they could be introduced to Cs site with relatively high efficiency. This seems that Al and Ga become Al^+ and Ga^+ in the crystal, respectively. The XRD analysis showed that the a-axis expands and the c-axis shrinks in the crystal as the impurity ratio increases for the samples measured in this study.

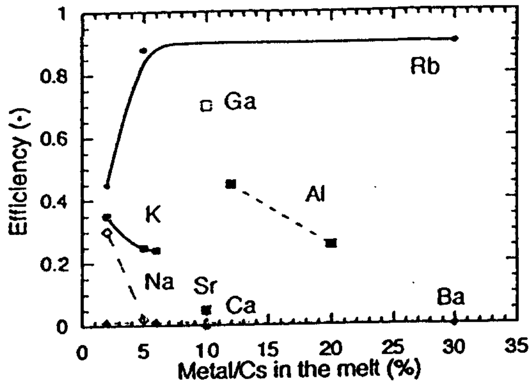

Figure 2. The doping efficiency of various impurities in CLBO crystal as a function of dopant concentration in the melt.

Effect of doping on the various properties has been studied. We found that the Rb doping could shorten CLBO's SHG cutoff wavelength (λc), for example the λc became 2 nm shorter for the crystal grown from 10 mole % Rb-doped (Rb/Cs = 0.1) melt. The Rb doping, however, has made CLBO more fragile. This was also the case for the K and Na doping. On the other hand, the Al doping could give rise to an enhancement of mechanical properties of CLBO. Figure 3 shows the Vickers hardness as a function of the Al/Cs ratio in the melt. Each data point represents an average value obtained from a number of indents on each sample. The hardness of undoped CLBO was 270 and 180 for (100) and (001) surfaces, respectively, while values for 1% Al-doped and 5% Al-doped CLBO were 290 and 310 for (100) and 220 and 230 for (001) surfaces. A similar hardness enhancement was observed for the Ga doping case. Actually, the Al-doped CLBO crystals have not been cracked even when they were the polycrystalline.

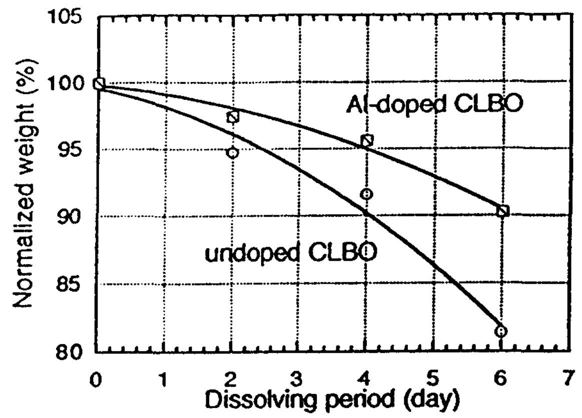

Figure 3. Vickers hardness of Al-doped CLBO (100) and (001) surfaces as a function of Al/Cs ratio in the growth melt.

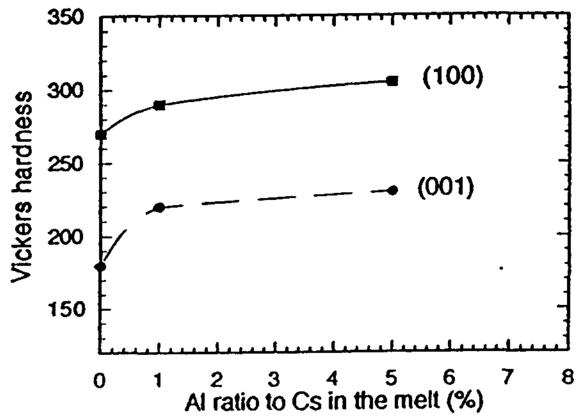

Figure 4. The normalized weight of undoped and Al-doped CLBO crystals dissolving in the solution of H_2O (20%) and glycerin (80%) as a function of dissolving period.

It was found that the hygroscopic nature of CLBO become less by the Al doping. The undoped and 2%Al doped CLBO crystals were dissolved in the solution of H_2O (20%) and glycerin (80%) in order to investigate the effect of doping on resistance against water. The samples have been dipped in the solution during experiment. Figure 4 shows the normalized weight of each sample as a function of dissolving period, showing that the Al-doped CLBO is less soluble than undoped CLBO.

Conclusions

We obtained the output energy of 230 mJ and 500 mJ at 213 nm and 266 nm, respectively, from the fundamental of 2200 mJ by using CLBO. It wa found that various metals can be used to dope CLBO. The Al doping could give rise to an enhancement of mechanical property of CLBO.

References

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UV Light Generation by $CsLiB_6O_{10}$ and Effect of Doping on Crystal Properties

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Outline

- Introduction
- Growth of CLBO
- NLO properties of CLBO
- Doping of CLBO
- Effect of thermal annealing
- Conclusion

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Introduction

UV NLO borate materials

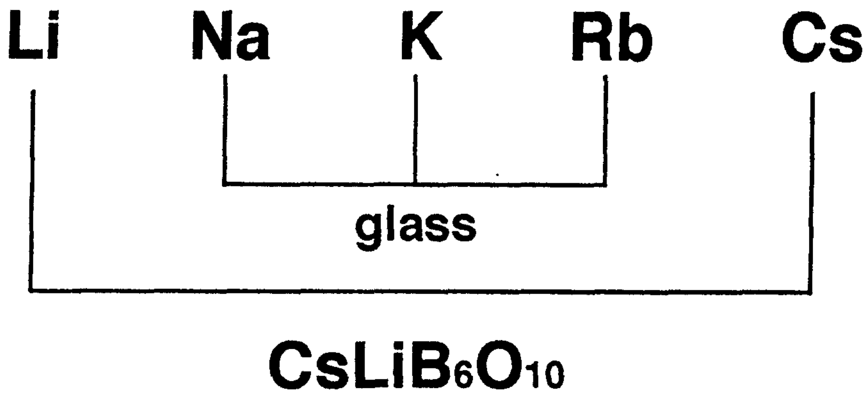
BaB_2O_4 (B_3O_6)
- large birefringence ~0.12
- α–β phase transformation

LiB_3O_5 (B_3O_7)
- small birefringence ~0.045
- difficulty in growth

CsB_3O_5 (B_3O_7)
- small birefringence
- congruently melting crystal

Research for new borate crystal

- Mixing every conbinations of alkali metals



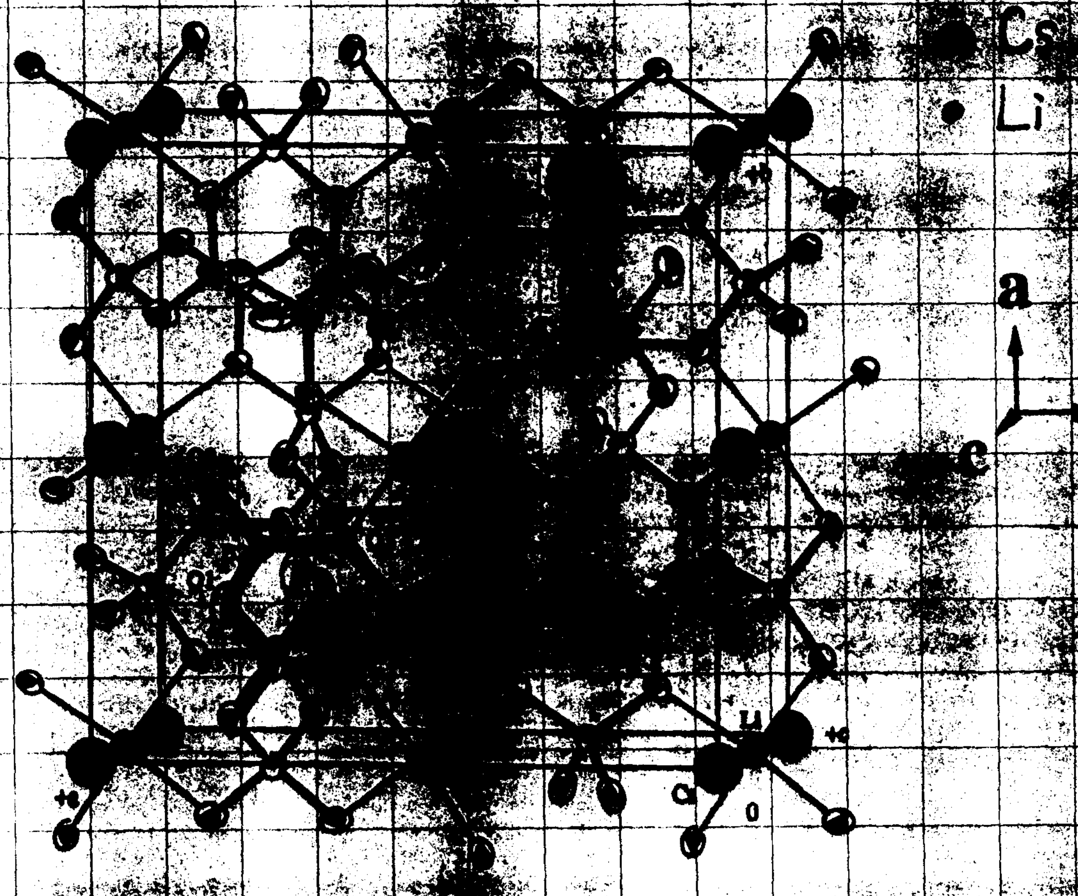
Features of CLBO crystals

- Transparent till 180 nm.
- It can be grown in a very large size in a short period (Ex. 14x11x11 cm^3 in 21 days). (congruent melt)
- It can generate 4th (266nm) and 5th (213nm) harmonics of Nd:YAG laser.
- The optical nonlinear coefficient is about same of LBO and a half of BBO but its angular and temperature allowances are about twice better than those of BBO.

Molec[illegible]

The structure of [illegible] atoms and four-coordinate Li atoms, and anion [illegible] of chains formed from B_3O_7 groups.
The Cs and Li atoms occupy the sites in the channel along the c axes alternately.

$CsLiB_6O_{12}$

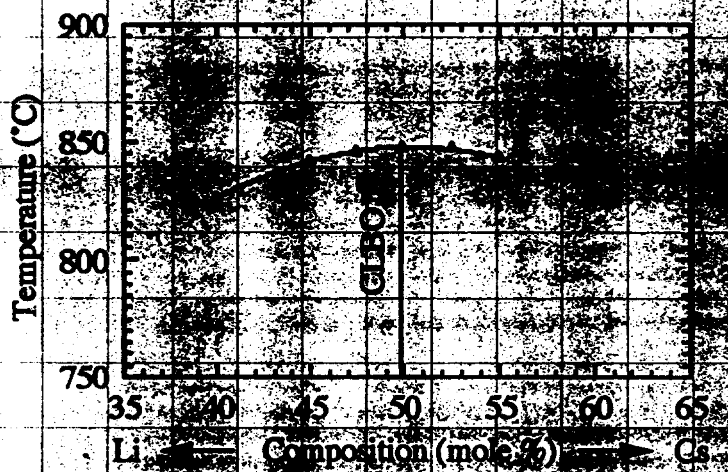


- Space G[illegible] $I\bar{4}2d$ (T[illegible])
- Point [illegible]m
- Latti[illegible]
- Calcul[illegible]
- Optical No[illegible]

... Cs_2O - Li_2O - B_2O_3 ternary

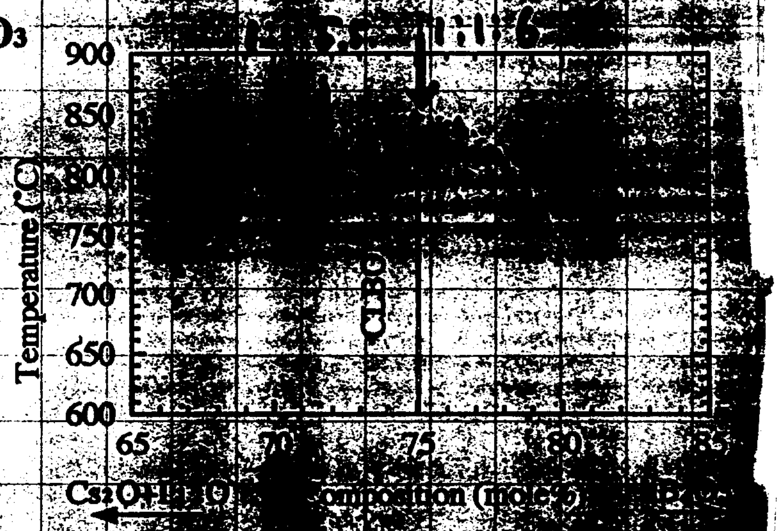
- Li_2O - Cs_2O binary

B_2O_3 const.



- (Li_2O + Cs_2O) - B_2O_3 binary

Li : Cs = 1:1 const.

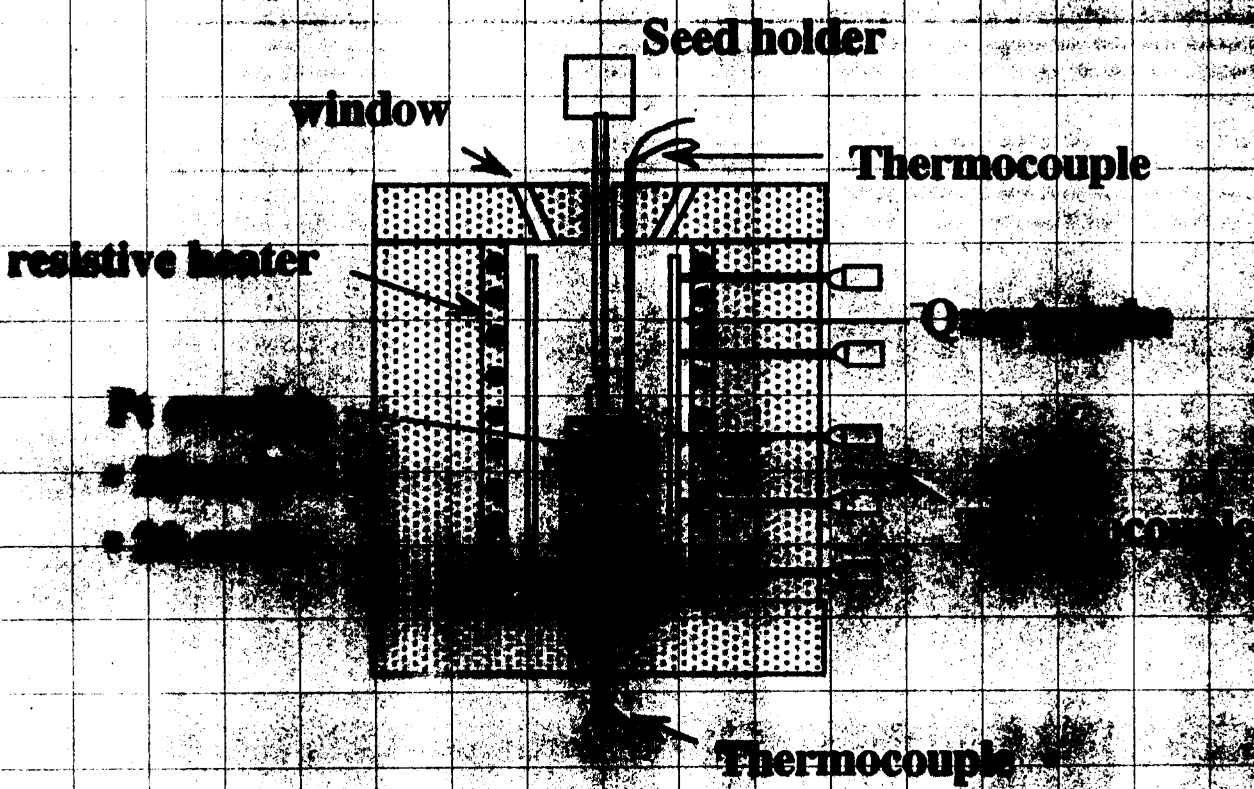


- CLBO can melt congruently at 848 °C.
- PDs show stoichiometric congruent point.

Grow[illegible]

- **Top Seeded Solution Gro[illegible]**

Furnace equipped with [illegible] resistance [illegible]



- **Starting material**

mixtutre of Cs_2CO_3, Li_2CO_3 and B_2O_3

ratio = 1 : [illegible] : 5.5

- **Growth temperature**

from 844.3 °C

- **Rotation ratio**

15 rpm

CLBO [illegible]

- Grown from flux method
- 14 x 11 x [illegible]xcxa)cm3
- 3 wee[illegible]th[illegible]
- 1.8 kg

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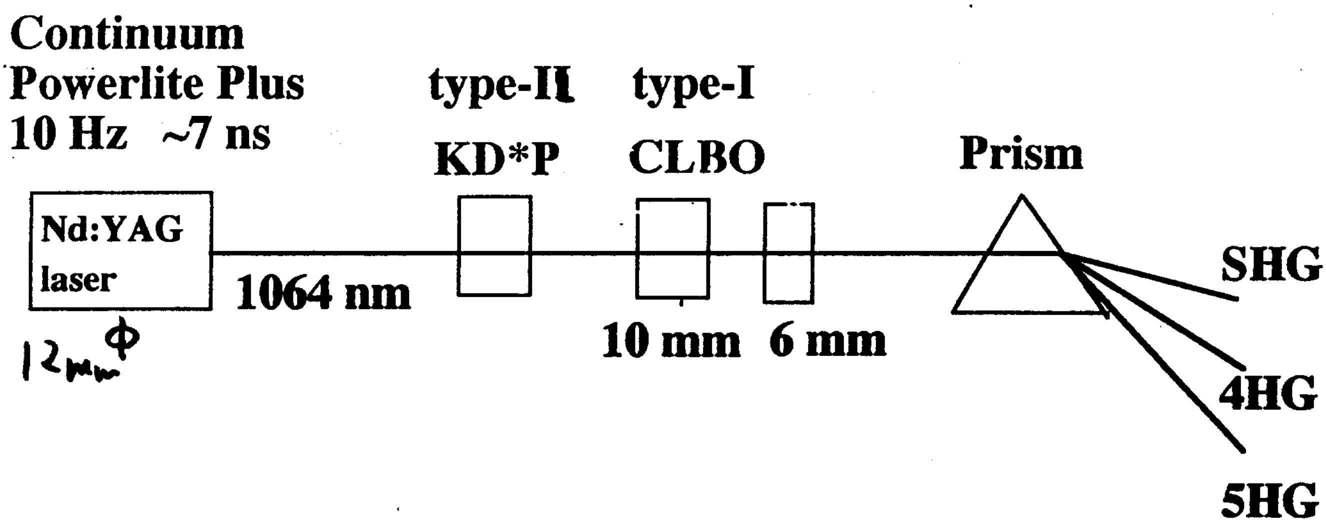
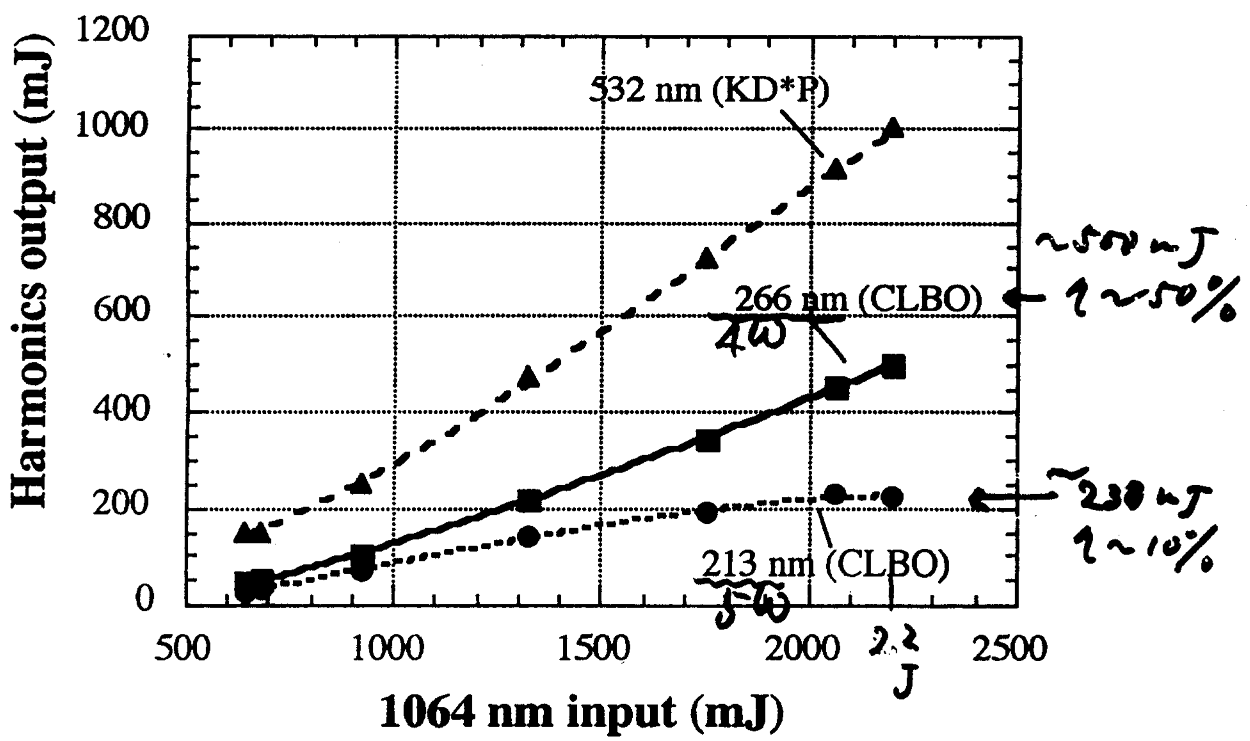
5ω

Fourth and
Fifth harmonic generation of Nd:YAG laser





230 mJ at 213 nm from fundamental of 2200mJ

η ~ 10%

Mechanical property of CLBO

• Vickers hardness

	(100)	(001)
CLBO	~260	~170
LBO	~450	~700

• Fragility of CLBO > LBO, BBO

It seems that particular care is needed in cutting and polishing CLBO single crystal, especially for the case of large size.

depend on { cutting
crystallinity of grown CLBO

Chemical property of CLBO

• Hygroscopy

KDP, CBO >> CLBO > BBO > LBO

Problems on CLBO

- fragility
- hygroscopic nature

⇛ change of refractive index

(negative lens effect)

↓

Cs atoms

- chemically active
- movable
(large equivalent isotropic displacement parameter)

Borate network

- high elasticity

↓ in order to overcome these problems

- Doping
- Coating
- Annealing

Doping of CLBO

Impurity doping ⟶ modification of properties

- Optical
  - shorter SHG cutoff wavelength
  - NCPM at typical wavelength
- Mechanical
  - stronger crystal
- Chemical
  - less hygroscopy

Group I element

Na, K, Rb

Group II element

Mg, Ca, Sr, Ba

Group III element

Al, Ga, In

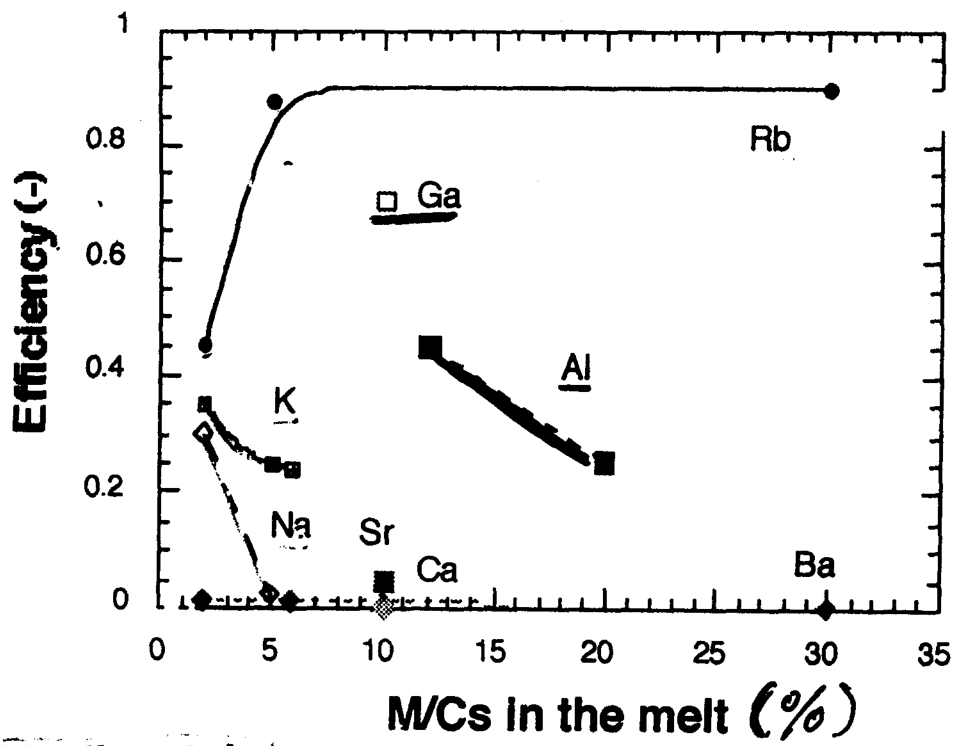
Doping of CLBO

Impurities $\xrightarrow{\text{replacement}}$ Cs site

- confirmed by four-circle X-ray diffractometer analysis

Doping efficiency

- ratio of dopant concentrations in the crystal and in the melt



Alkali metals

Rb > K > Na ionic radius

Alkali earth metals

low efficiency oxidation number 2+

Group III elements

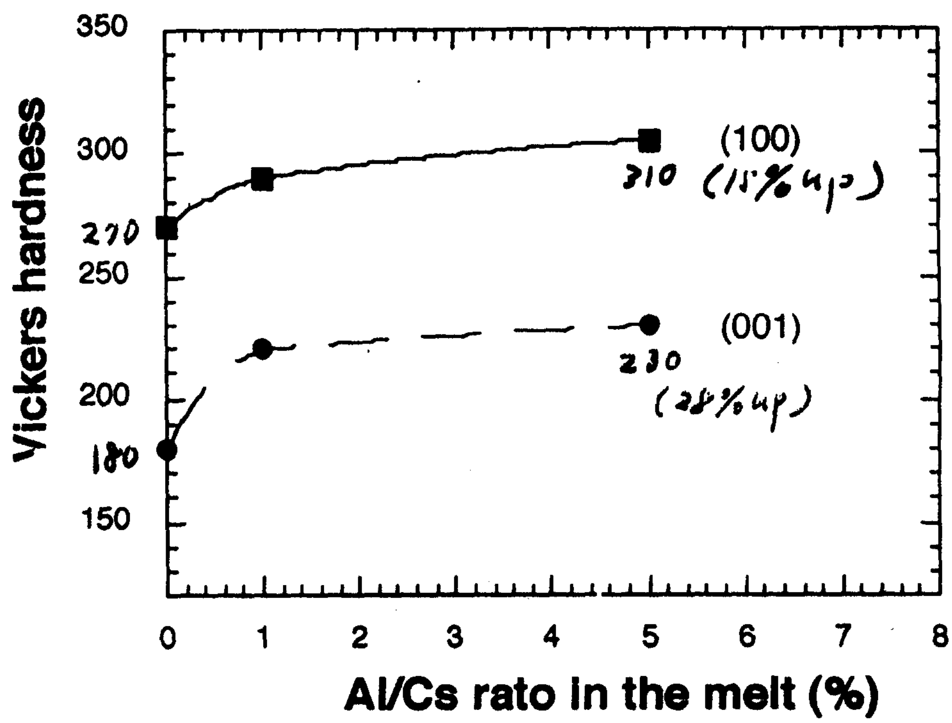
high efficiency Al^+ Ga^+ ? AlO GaO ?

Cs site

Effect of doping on mechanical property

Rb, K, Na doping ——→ more fragile

Al doping ——→ enhance mechanical property



Al-doping ——→ less crack

improve Vickers hardness

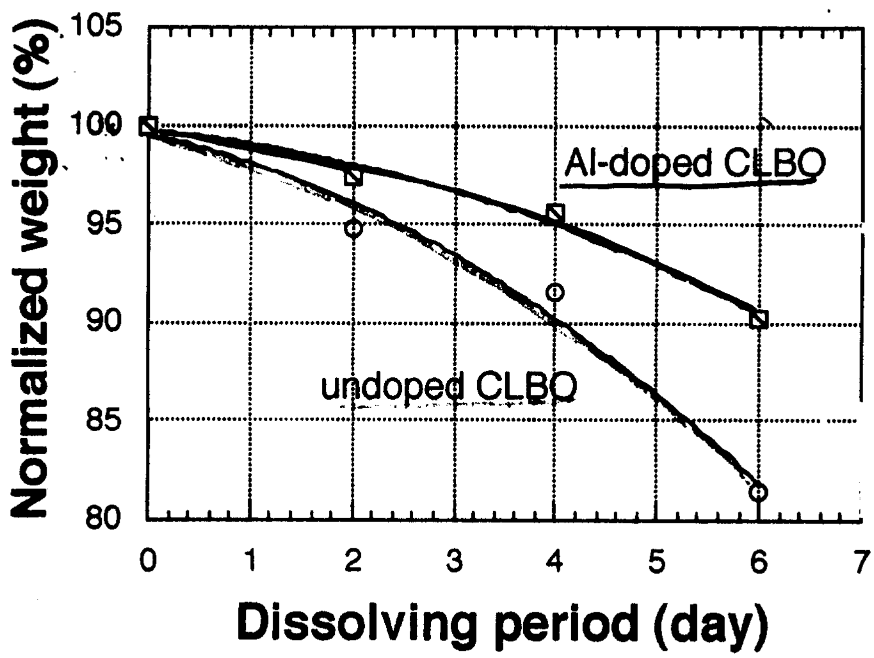
Effect of doping on chemical property

Hygroscopic nature ——→ Cs atom + α

Investigation of solubility in water

undoped CLBO	**dipping**	**H_2O (20%)**
2% **Al-doped CLBO**	——→	**glycerin (80%)**

~1.8g



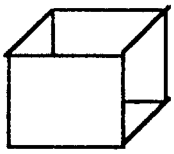
Al-doping ——→ less solubility in water

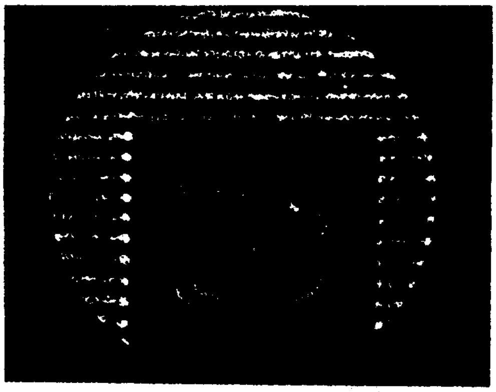
Effect of annealing on CLBO

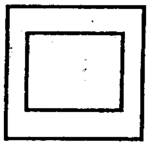
Laser interferogram in transmission of CLBO

After index change

beam pattern



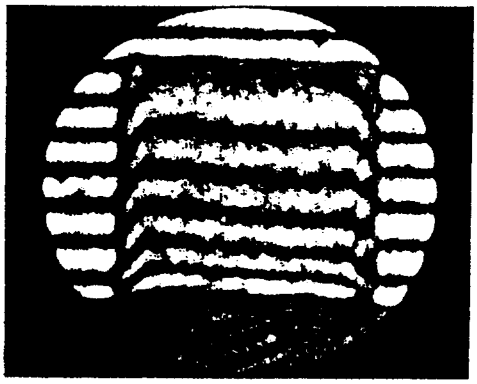


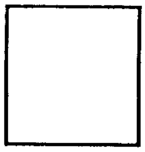


12×12 mm²

- induced by mechanical stress
- grow in moderate temperature and/or high humidity
  ~40~90 °C ~70%

After annealing at 200~300 °C





- keep sample at low temperature and low humidity
  ~20 °C
- keep annealing at ~120 °C

Change of refractive index in CLBO

equivalent isotropic displacement parameter B_{eq}

by four-circle X-ray diffractometer analysis

↓

stability of the atom

CLBO

Cs	2.4
O(1)	1.9
O(2)	1.1
B(1)	0.8
Li	1.3

α-BBO

Ba	0.9
O(1)	1.2
O(2)	1.1
B	1.5

CBO

Cs	1.9
O(1)	1.5
O(2)	1.0
B(1)	1.1

LBO

Li	1.6
O(1)	0.6
O(2)	0.7
B(1)	0.5

Cs atoms in CLBO —(large B_{eq})→ movable

↓

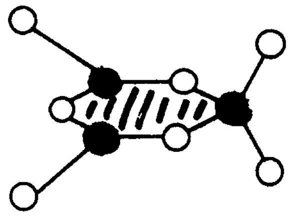
give elasticity to borate network

↓

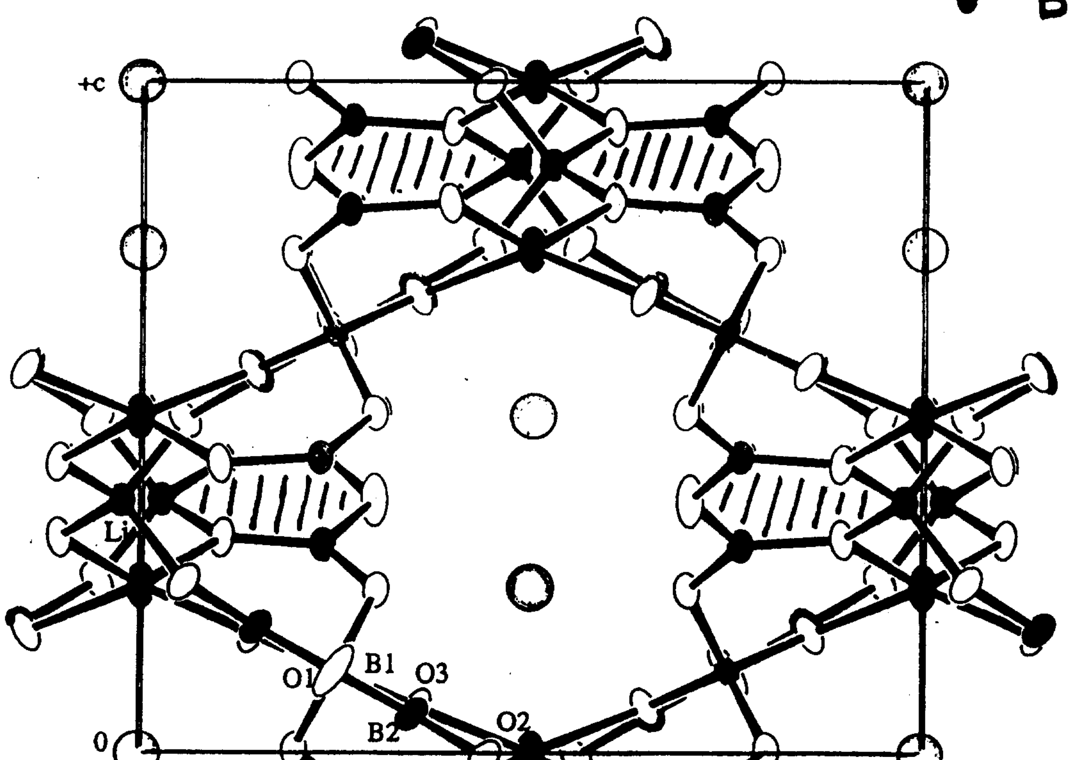
change of refractive index

結晶構造

・4軸単結晶X線回折による構造解析



基本構造 B_3O_7



結晶構造図（a 軸方向）

Conclusions

1. We have discovered $CsLiB_6O_{10}$.

   Stoichiometric congruent point

   Excellent UV NLO properties

2. High efficient harmonics has been obtained by CLBO.

   1.55 J at 532 nm from fundamental of 3 J

   500 mJ at 266 nm from SHG of 1000 mJ

   230 mJ at 213 nm from fundamental of 2200 mJ

3. Various metals can be used to dope CLBO.

   Al doping

   Enhancement of mechanical and chemical properties

4. Effect of annealing on CLBO has been investigated.

   Thermal annealing can restore the refractive index of CLBO.