Preparation and Properties of a Complex Crystal for Nonlinear Optical Applications: Cadmium Mercury Thiocyanate

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Abstract:

A complex nonlinear optical crystal Cadmium Mercury Thiocyanate with size 18*18*20mm^3 was grown. It possesses chemical stability below 247℃, no cleavage, and high mechanical strength. Blue light second harmonic of diode laser was realized.

Summary:

Cadmium Mercury Thiocyanate ($CdHg(SCN)_4$,CMTC) crystal is one of the most efficient Nonlinear Optical crystals among complex crystals. This paper reported the growth, structure analysis and charaterization results of the crystal.

Large single crystal CMTC with size 18*18*20mm^3 was grown from water/KCl /NaCl mixture solvents by using slow cooling method for the first time. A moderate solubility 100g/1000ml and positive temperature deperature dependence occurred in such a solution system. We redermined the crystal structure of CMTC. CMTC belongs to tetragonal system. The crystallographic parameters are: a=11.487(3)A, c=4.218(1)A. One CMTC molecule was constituted of two distorted tetrahedrons: Hg-S4 and Cd-N4. It was very interesting in the molecular structure that these two distorted tetrahedrons were connected by a conjugated charge bridge-S=C=N-, and finally form a charge transfer system, which was believed to be and essential factor to induce high hyperpolarizabilites.

CMCT crystal has no hygroscopical effects at atmosphere circumstance and room temperature. Thermal analysis showed that it is stable below decomposition temperature 247℃. During the crystal processing, no cleavage was observed.

CMTC crystal is transparent in a wide range from violet to IR. The UV transparency cut-off occurred at 380nm, and the first IR absorption band occurred at 2350nm,

Two principal refractive indices of CMTC crystal were determined by using V-prism method. The measured data were then fitted to the Sellmere equations as follows,

$$n_0^2 = 3.661861+0.077588/(\lambda^2 - 0.069737)-0.04548\,\lambda^2$$

$$n_e^2 = 2.950921+0.041337/(\lambda^2 - 0.058791)-0.0075921\,\lambda^2$$

It can be drown from the dispersion equation that CMTC is phase matchable down to cutoff wavelength for both types of Phase Matching.

Recently, bright blue light blue light second harmonic of GaAlAs diode laser was realized on CMTC PM I frequency doubling device with input power lower than 500mW.

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Application of Compact Blue—Green Lasers

- optical recording
- imaging and printing
- optical communications
- surgery
- full—colour displays

Materials for Compact Blue-Green Lasers

- ◆ Semiconductors ⟨ II-VI ZnSe...
  GaN

- ◆ Nd:Laser (YAG, YVO_4, SFAP) + NLO Crystal (KTP etc.)
  NdYAB
- ◆ IR LD + NLO Materials (Bulk Crystals, Waveguide (QPM))
  MHBA
  CMTC
- ◆ Upconversion Fiber Lasers

1 Materials for blue-green compact laser

- ◆ Semiconductors--- II-VI ZnSe…, GaN
- ◆ Nd:Laser (YAG, YVO_3, SFAP)+NLO Crystal (KTP etc.)
- ◆ IR LD + NLO Materials (Bulk Crystals, Waveguide (QPM))
- ◆ Upconversion Fiber Lasers

Diode Pumped High Efficiency Nd:YVO_4/KTP Laser

Conversion Efficiency 24%

* Characters of III-V series diode laser
  - $\lambda < 1000$ nm
  - low power
  - beam dispersion

* Requirements of NLO crystal materials for LD SHG
  - d_{eff}: 1-3 orders higher than that of KDP
  - UV cut-off $\leq$ 400 nm
  - phase matching (NCPM)
  - easy to grow

Organic NLO Crystal Materials

Advantages:

- Very large second-order nonlinearities ($\chi^{(2)}$);
- Ultrafast response time;
- High damage threshold;
- Extreme diversity of structure;
- Flexibility of material design.

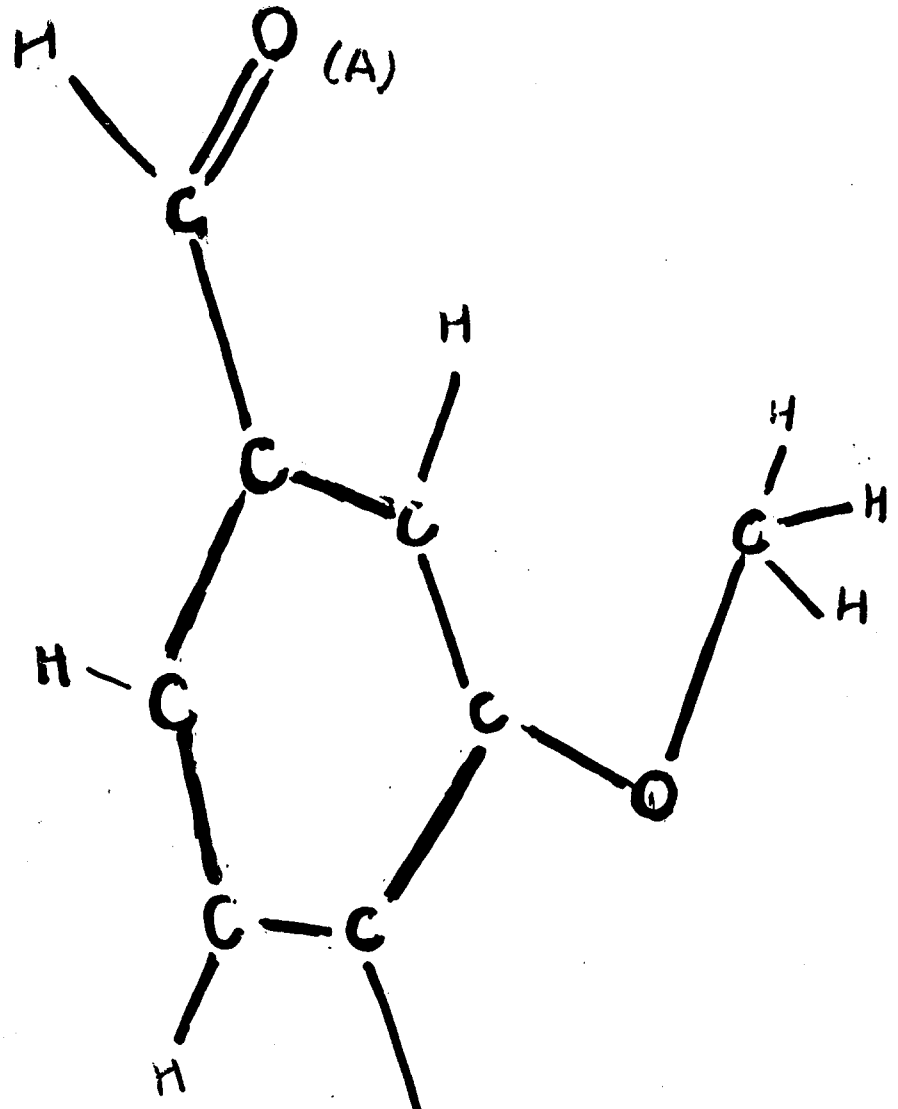
Disadvantages:

- Optical transmission is limited on the short-wavelength side;
- Temperature dependence of physical properties is generally large;
- Crystal growth is difficult.

2 Generation of violet-blue light by SHG of infrared laser diode using new organic crystal --- MHBA

3-Methoxy-4-Hydroxy-Benzaldehyde (MHBA)

- Mixed solution growth 70X40X15mm^3 MHBA Single Crystal
- $d_{13}=25d_{36}^{KDP}=21pm/V$
- $\Delta n<0.29$
- $\Delta E_g=370nm$
- Optical damage threshold $>2GW/cm^2$
- Violet-blue (404.5nm) SHG of diode laser (809nm) by using MHBA for the first time



MHBA OH (D) $C_8H_8O_3$

3-Methoxy-4-hydroxy-benzaldehyde

3-甲氧基-4-羥基苯甲醛

Blue-violet SHG output of diode laser

Pump source: 809-817nm, multimode, cw GaAlAs diode laser

Input power: 1W

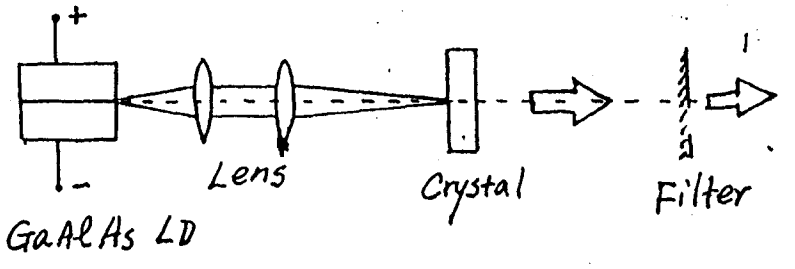
Conversion efficiency 3×10^{-6}

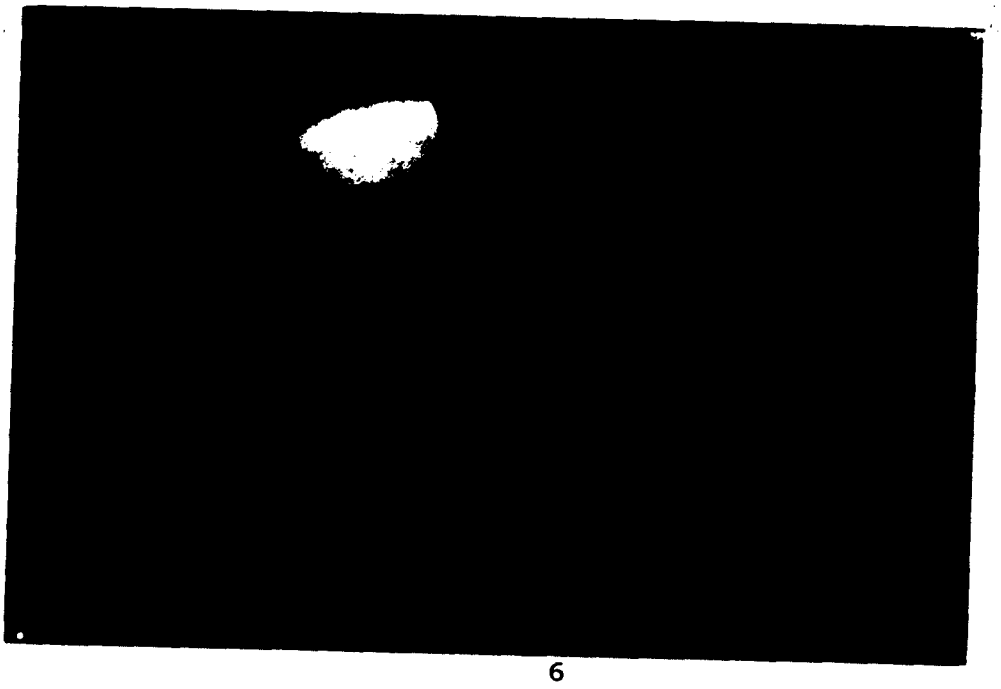
Blue SHG output: 3μW

Sample orientation: $\Theta=90°, \phi=15°$(PM I)

Device thickness: 5mm

Fig.





◆ **Direct SHG of laser diode**

SHG of IR LD ---Bulk ($KNbO_3$, KLN, MHBA,APDA)

---Waveguide (LT,LN,KTP, polymer)

NLO crystals for SHG of LD:

---Inorganic , Organic

Organometallic crystals ?

Cadmium Mercury Thiocyanate **(CMTC)**

MHBA: 3-Methoxy-4-Hydroxy-Benzaldehyde, --- > **3μW**

X.T.Tao, et al, Appl. Phys. Lett. 60(12),1415(1992).

APDA: 8-(4'-acetylphenyl)-1,4-dioxa-8-azaspirol[4.5]decane, **2μW**

M.Sagawa, et al, Appl.Phys.Lett. 66(5),547(1995)

3 A Organometallic Complex Crystal for Blue-Violet Light Generation---CMTC

- Direct SHG of laser diode
- Crystallographic properties of CMTC crystal
- Crystal growth
- Thermal properties
- Linear optical properties
- Nonlinear optical properties
- Blue-Violet light SHG output
- Conclusion and prospects

◆ Crystallographic properties of CMTC crystal

CMTC: Cadmium Mercury Thiocyanate

Chemical formula: $CdHg(SCN)_4$

Space group: I4

Cell parameters: a=11.4403Å

c=4.2043Å

◆ Crystal growth

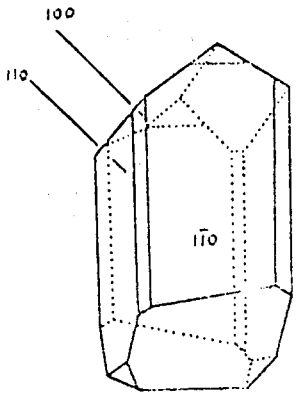
Method: slow cooling method

Growth duration: 30 days

Crystal dimensions: $15*15*20mm^3$

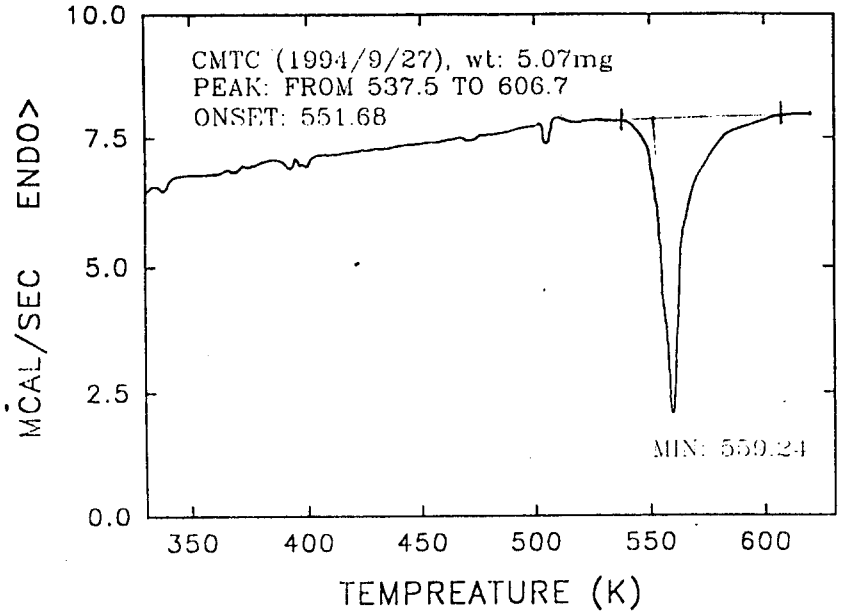
Crystal habit:

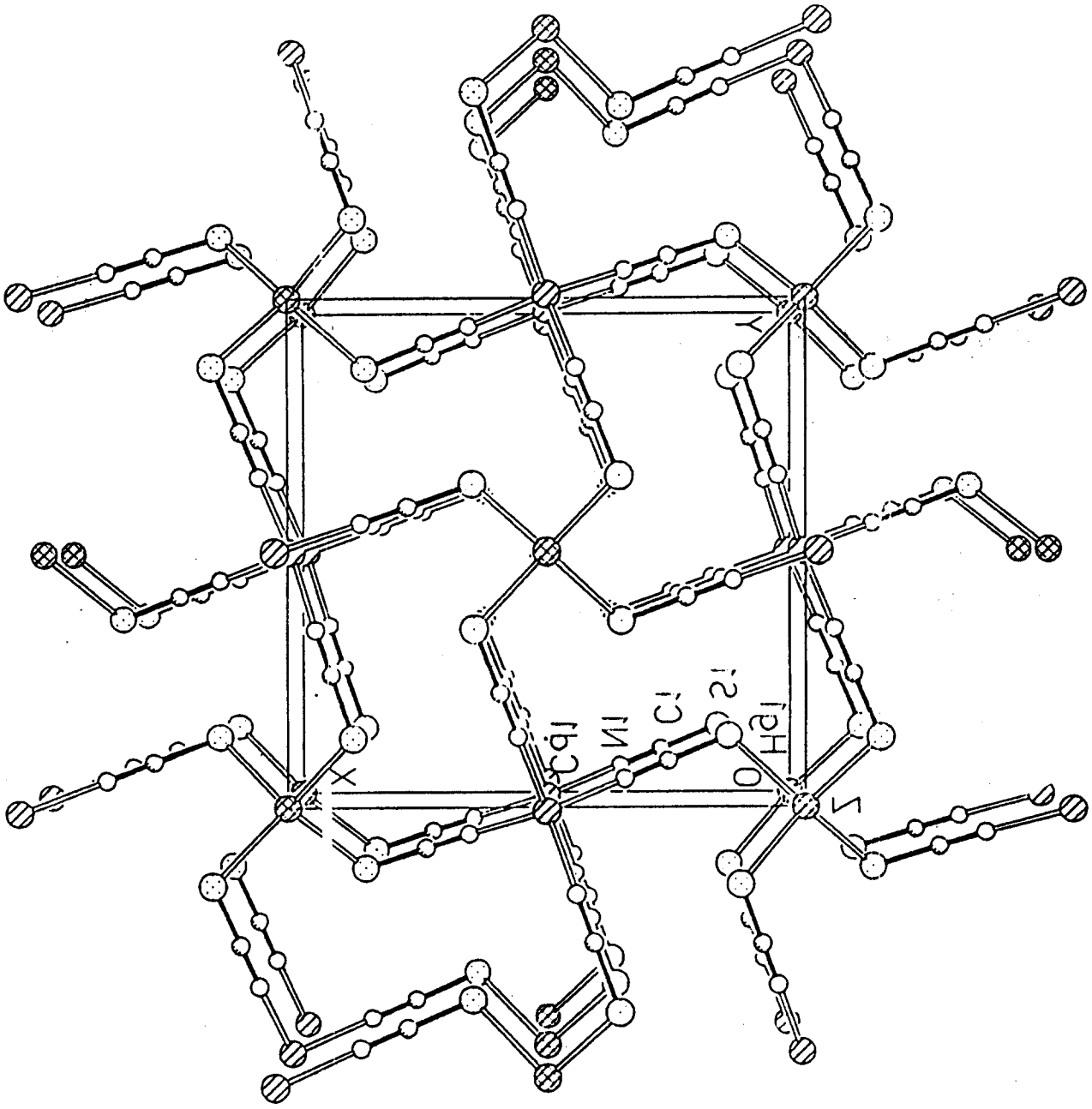
FIG.



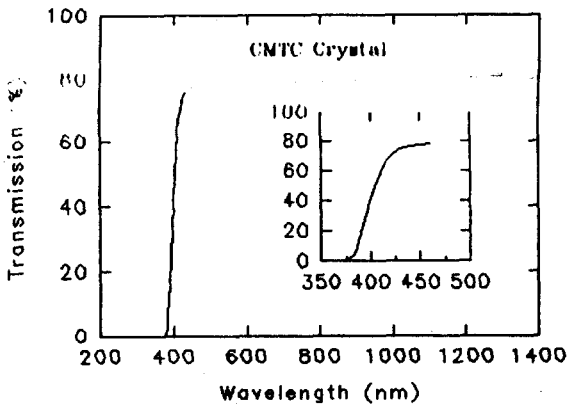
◆ Thermal properties

DSC:(Decomposition temp.: **551K**)




Y
X
Z
Cd
N
Cl
S
Hg
O
N

◆ Linear optical properties: Transmission:

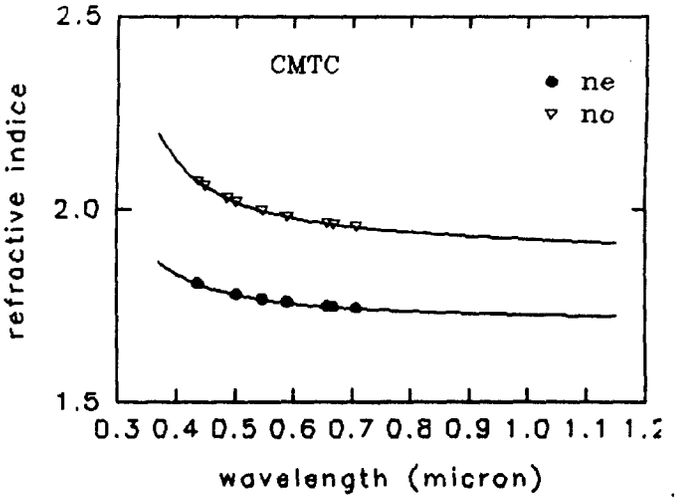


Transparent from: 0.4 2.3μm

Refractive index determination:

Measured refractive indices

Lamda (μm)	n_o	n_e
0.4358	2.072967	1.80686
0.4471	2.061942	---
0.4861	2.028454	---
0.5015	2.019460	1.77857
0.5461	1.996982	1.76676
0.5876	1.981857	1.75859
0.5893	1.981392	1.75834
0.6563	1.963567	1.74889
0.6678	1.962064	1.74757
0.7065	1.954334	1.74392

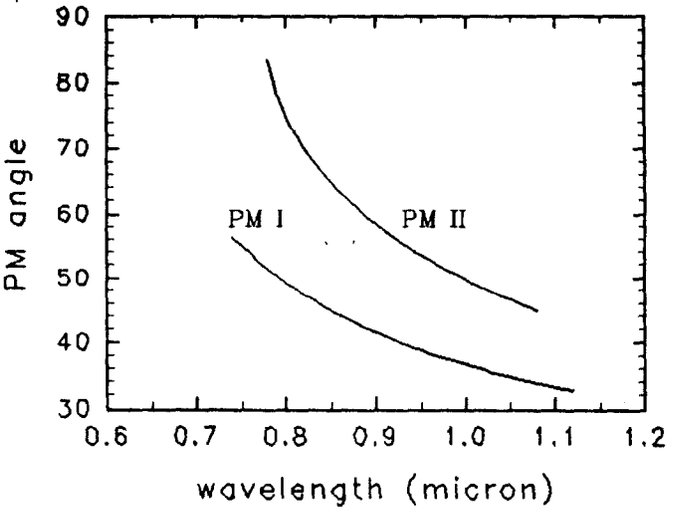


Sellmeier Equation:

$n_o^2=3.661861+0.077588/(\lambda^2-0.069737)-0.045487\lambda^2$

$n_e^2=2.950921+0.041337/(\lambda^2-0.058791)-0.007592\lambda^2$

Phase matching properties



PM region type I:0.78μm-

Type II:0.778μm-

◆ Nonlinear optical properties

NLO coefficients:

$$\begin{bmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & -d_{15} & d_{14} & 0 \\ d_{15} & -d_{15} & 0 & 0 & 0 & d_{14} \end{bmatrix}$$

Bergman (1970): Wedge method

$$d_{15}=d_{31}=(1.3\pm0.1)d_{33}(LiIO_3)$$

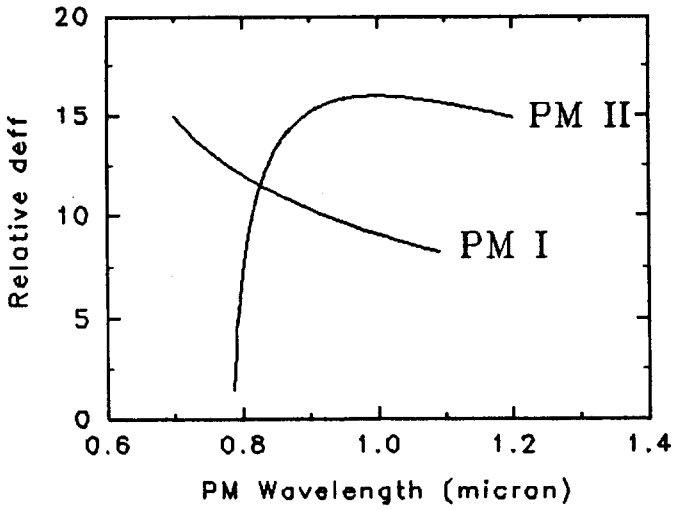
$$d_{14}=d_{36}=(0.3\pm0.1)d_{33}(LiIO_3)$$

Effective NLO coefficient:

$$d_{eff}^{I}=\sin(\theta)(d_{14}\sin(2\phi)+d_{15}\cos(2\phi))$$

$$d_{eff}^{II}=\sin(2\theta)(d_{14}\cos(2\phi)-d_{15}\sin(2\phi))$$

Type II CMTC SHG device at about 950nm possess the nearly greatest effective NLO coefficients.



◆ Blue-Violet light SHG output

Violet light generation:

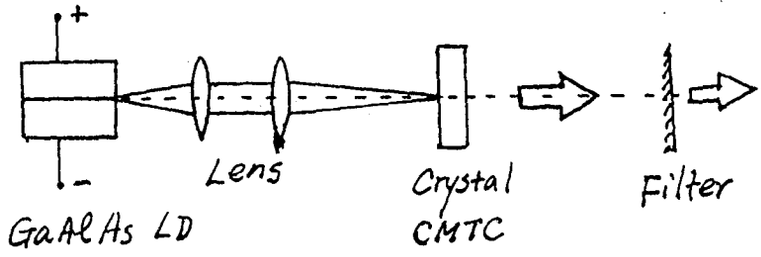
Input: cw GaAlAs laser diode

λ=809nm,

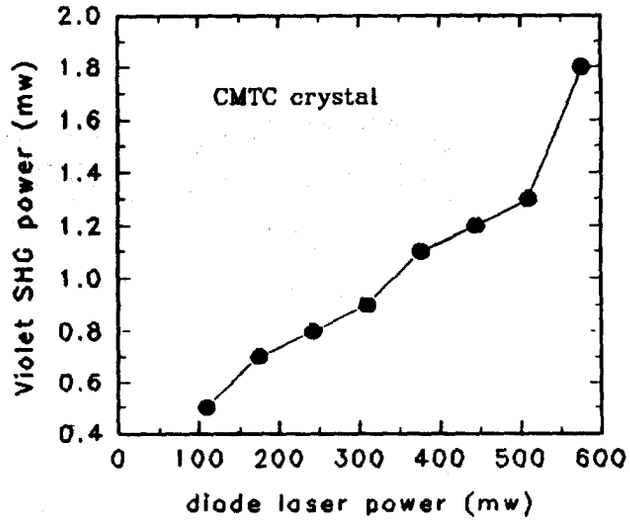
CMTC crystal SHG device:

- PM I, θ=48.4°,ϕ=0°
- PM II, θ=72.74°,ϕ=45°

FIG. Experimental arrangement for SHG of LD



Violet light SHG output vs. power of LD



Blue light generation

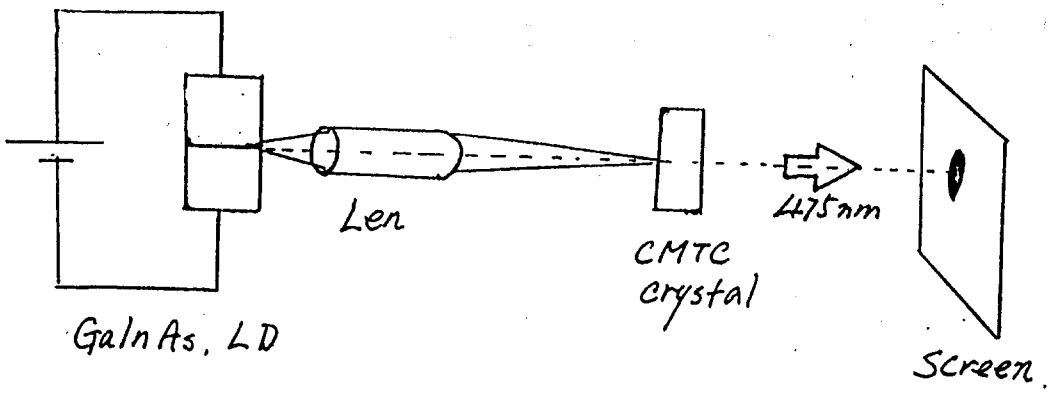
Input: cw GaInAs laser diode, $P^{th} < 40mw$

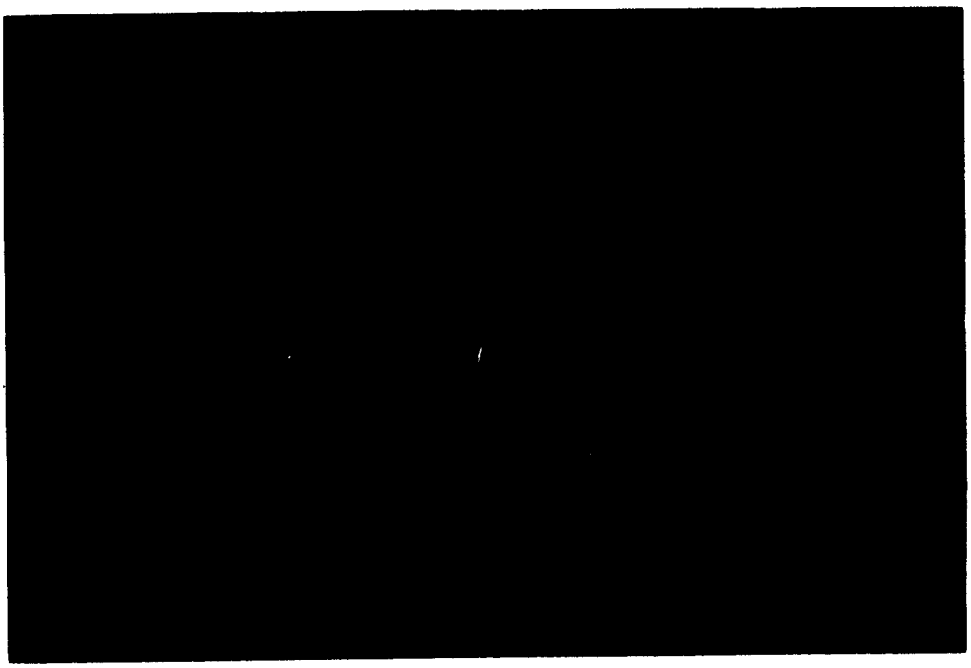
$\lambda = 950nm$,

SHG device: CMTC crystal, $\theta = 34.32°, \phi = 0°$

Sample thickness: 2.9mm

Fig.





◆ Conclusions and Prospects

Conclusions:

1 Growth and characterization of CMTC crystal

a) Growth from solution

b) No hygroscopic

c) High decomposition Temp.: 551K

d) Transparent at blue-violet region (0.4---2.6μ)

e) Phase matchable from 0.78μm

f) Laser Damage Threshold >200MW/cm^2

2 Blue-violet light generation of diode laser by using single pass scheme

a) 1.8 mw violet light (404.5nm) SHG of cw GaAlAs laser diode

b) bright blue light (475nm) SHG of cw GaInAs diode laser with input power less than 50 mw

Prospects on CMTC crystal:

1 High efficiency Type II PM SHG output of GaInAs diode laser is expected owing to great effective NLO coefficient.

2 Conversion efficiency enhancement of blue violet light generation of diode laser by using external resonant cavity scheme.

3 High efficiency blue light generation by Intra-cavity SHG of 946nm diode pumped Nd:YAG laser