Data Sheet 707

QUANTUM TECHNOLOGY, INC.

Non-Linear Optical Properties of D-CDA Crystals

Physical Properties of D-CDA:

Deuterated cesium dihydrogen arsenate, $Cs\,(D_{1-x}\,H_x)_2\,AsO_4$, is commonly designated as D-CDA or CD*A. It crystallizes in the tetragonal system, space group $\bar{4}2m$ and is isomorphous with KDP. It is a negative uniaxial crystal. It has a melting point of 240°C but, decomposes slowly when heated above 150°C, releasing water vapor. It is mechanically fragile due to the weak hydrogen bond and is also thermally sensitive. Thermal shock exceeding 5°C/min may crack or shatter the crystal. The density of D-CDA crystal is 3.45 gm/cm³. Its Curie temperature is 212.4°K and has a hardness of about 2 on the Mohs scale. It is extremely soluble in water, about 3000 gms/liter at room temperature. Thus it is very hygroscopic and must be stored in a dessicator or operated in hermetically sealed cells filled with dry nitrogen. It requires special handling and polishing techniques.

TABLE 1
PHYSICAL PROPERTIES

No.	Property	Value
1	Thermo-optic co-efficient	'O' ray 26.2 ppm/°C
2	Thermo-optic co-efficient	'E' ray 19.2 ppm/°C
3	Optical absorption	at 1064nm < 0.6%/cm
4	Thermal co-efficient of expansion	'z' axis 51 ppm/°C 'a' axis 8.7 ppm/°C
5	Thermal conductivity	0.015 W/cm °C
6	Temperature co-efficient of birefringence	5.25 ppm/°C
7	sp heat at 100°C	0.1290 cal/gm °C
8	90° phase match temp.	110°C for 95% D-CDA

Single crystals of D-CDA are grown from saturated heavy water (D_2O) solutions by controlled slow cooling of the solution. Crystals with two levels of deuteration are normally available, 95% and 98%. The deuteration level represents the percentage of hydrogen atoms in cesium dihydrogen arsenate (CsH_2AsO_4) that are replaced by deuterium $Cs(D_{1-x}\,H_x)_2\,AsO_4$. Single crystals of D-CDA grown in heavy water have improved IR transmission (260 to 1100 nm) compared to crystals of CDA, which are transparent only upto 800 nm. Also, the deuterated crystals have a higher electro-optic constant r_{63} and non-linear susceptibility constant d_{36}.

Nonlinear Optical Properties:

Since 1970 Quantum Technology Inc. is the **ONLY** commercial producer of high grade, optical quality single crystals of D-CDA. It has very interesting non-linear optical (NLO) properties, finding the most use in non-critical phase matching of Nd:YAG lasers at 1064 nm.

The non-linear optical (NLO) properties and applications of crystal D-CDA have been extensively investigated. The non-linear coefficient in the phase matched directions is given by,

$$d_{ooe} = d_{36} \sin\theta \sin 2\phi \qquad \text{(type I)}$$

When the crystal D-CDA is cut such that $\phi = 45°$ and $\theta = 90°$, then $d_{ooe} = d_{36}$. The crystal is called non-critically phase matched and maximum efficiency is obtained with zero beam off.

When the D-CDA crystal is oriented such that $\phi = 45°$ and $\theta = 81°$, then $d_{ooe} = (0.98)\, d_{36}$ the effective non-linear coefficient is slightly decreased, thereby lowering the efficiency.

At 1064 nm, $d_{36} = 0.58$ pm/V. The d_{36} NLO coefficient of D-CDA is 1.03 times that of D-KDP (Type II) at 1064 nm. For the case of perfect phase matching with a single mode pump and without any Fresnel losses, the harmonic power (P_2) is given by,

$$P_2 = P_1 \tanh^2 (\ell / \ell_s)$$

where $\ell_s = [1 / (8\ \pi^2 / n_{10}\ \lambda\ )]\, d_{36}\, E_o$. $E_o = 820$ esu. The thermo-optic coefficient $(dn/dT) \times {}^1/n$ is minus 26.23 ppm/°C for the o-ray and minus 19.23 ppm/°C for the e-ray at both 1064 nm and 532 nm.

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It has a moderate birefringence ($n_o - n_e = 0.016$) at 1064 nm and low dispersion allowing only type I phase matching. The variation of birefringence with temperature over the range 30° to 55°C is dB/dT = 5.25 ppm/°C. It is useful for non-critical phase matching (NCPM) of Nd:YAG laser (1064 nm), has a transparency range from 260 to 1100 nm and can be angle phase matched or temperature phase matched for Nd:YAG, Nd:YLF, Nd:GSGG and Nd:Glass lasers. It has a damage threshold equal to that of D-KDP crystal of 350 MW/cm² for 10 ns pulse widths.

D-CDA Refractive Indices:

The refractive indices are given by a two term Sellmeier equation:

$$n^2 = 1 + \frac{\lambda^2 A}{(\lambda^2 - B)} + \frac{\lambda^2 C}{(\lambda^2 - D)}$$

where A, B, C and D are given in Table I.

TABLE II

Parameter	A	B	C	D
n_o	1.4029	0.0132	0.1465	24.01
n_3	1.3495	0.0122	0.0628	25.0

where λ is expressed in micrometers.

Typical refractive indices of D-CDA at different wavelengths are given in Table II.

TABLE III

Wavelength nm	n_o	n_e
514	1.5736	1.5542
535	1.5717	1.5522
633	1.5657	1.5467
694	1.5629	1.5445
1064	1.5529	1.5369

Non-Critical Phase Matching with D-CDA:

Harmonic generation by 90° (temperature tuned or non-critical) phase matching is often much more efficient than angle tuned (critical) phase matching. Beam walk-off that occurs with angle phase matching is eliminated with 90° phase matching. Also, the finite acceptance angle of a non-linear crystal which comes about because beams that are focussed at an angle into the crystal will have components that are not properly phase-matched. This is a much smaller limitation with NCPM.

One of the most attractive features of crystal D-CDA is that it can be non-critically phase matched with pulsed Nd:YAG, Nd:YLF and Nd:Glass lasers for type I operation. Crystals LBO and $KNbO_3$ (B cut) can also be NCP matched with the above lasers, but are limited in their size (typically 5 X 5 mm²), that is available. Crystals of D-CDA are available in cross-sections that are as large as 30 X 30 mm² and 40 mm long. These sizes are especially useful for handling large aperture lasers.

For CDA (non-deuterated isomorph), the NCPM temperature is about 45°C at 1064 nm. It has a high absorption at 1064 nm (3% per cm) and is thus useful for only low average powers of upto 10 watts. On the other hand, for 95% D-CDA crystal the NCPM temperature is 120°C and absorption 0.9% per cm and for 98% D-CDA crystal it is 120°C with absorption around 0.6% per cm. For high average input power, over 30 watts, 98% D-CDA crystals are used because of lower absorption.

Under non-critical phase matched conditions D-CDA crystal has a very high angular acceptance, 76 mrad-cm and zero beam walk-off. For type I second harmonic generation (SHG), at 1064 nm, D-CDA has a high peak power damage threshold of 350 MW/cm² and a high fluence damage threshold of 26 Joules/cm². With a 30 mm long crystal, doubling efficiencies of over 55% are obtained with flash lamp pumped Nd:YAG and Nd:GSGG lasers. Also, the input and output beams are collinear making tripling (THG) straightforward.

Further advantages to using D-CDA are a very large temperature half width of ± 3.5°C and a very low sensitivity to angular changes (only 10% of that for D-KDP type II). This makes angular alignment and thermal control of the D-CDA crystal less critical than with a type II D-KDP crystal.

A disadvantage to using D-CDA under NCPM conditions is the temperature at which it is operated. Its NCPM temperature of 120° C is very close to the temperature (150° C) at which slow decomposition takes place. Thus, there is a possibility that the temperature at a localized point may exceed 150°C, due to hot spots in the beam especially in the multi-mode condition. This could damage the crystal resulting in failure of the doubler. This problem is overcome by a combination of angle phase-matching ($\theta = 84°$, $\phi = 45°$) and temperature phase-matching ($\approx 60°$ C) with slight decrease in angular acceptance.

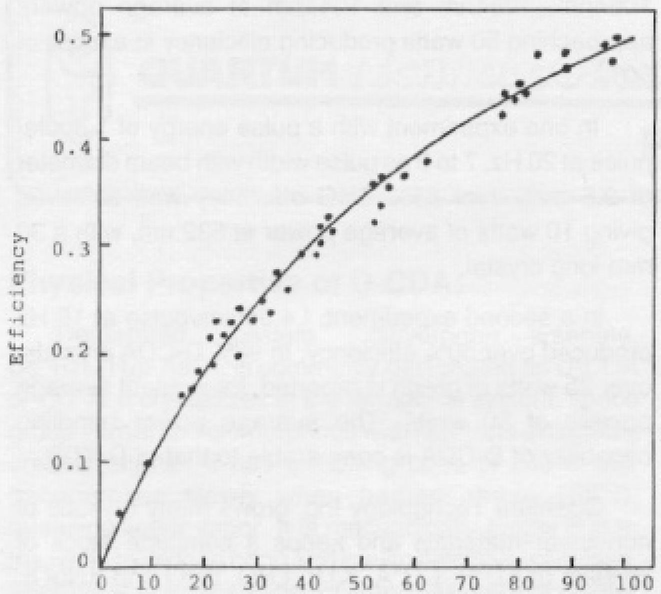

Fig. 1 Density MW / cm²

Efficiency vs peak power density with 25mm long D-CDA

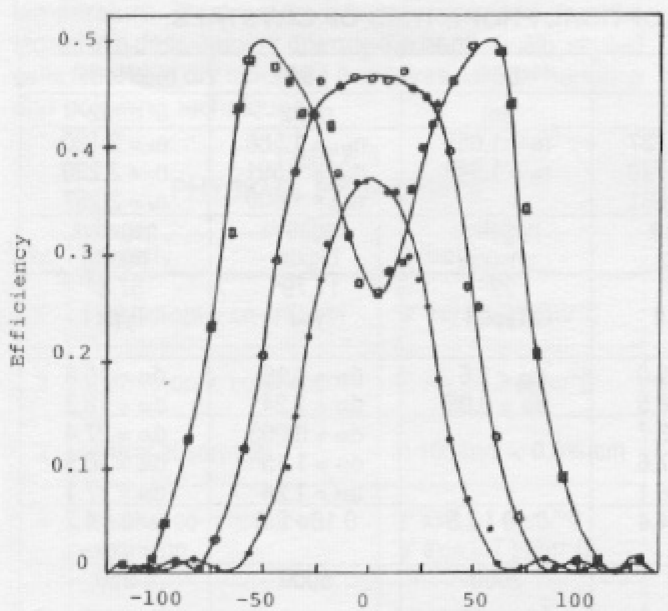

Fig. 2 mrad

■ Temp. 108°C ● Temp. 110°C • Temp. 112°C

Efficiency vs angular deviation from 90° phase matched condition.

Angle phase matching with D-CDA:

The relationship between angle and wavelength for SHG of 1064 nm with a D-CDA crystal is shown in figure 3. The phase matching angle increases by 0.08 per °C. Crystal D-CDA shows highly assymetrical angular phase matching tolerance. Angular tolerance in θ direction (phase matching at 80° angle) is ten times larger than in the ϕ direction. This high degree of angular assymetry requires beam shaping techniques to obtain optimum efficiency.

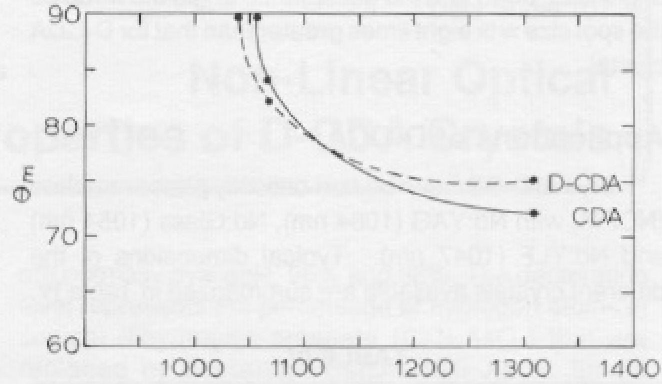

Fig. 3 Fundamental Wavelength (nm)

Phase match angle vs wavelength

Crystal CDA (non-deuterated isomorph) oriented at an angle 85° with respect to the optic axis critically phase matches for 1064 nm at room temperature. For D-CDA (95%), this angle is 81° for room temperature operation at 1064 nm. For high powers, it is customary to orient the D-CDA crystal rod at 84° angle for temperature around 65°C to insure high reliability and longer life of the SHG device. This angle decreases as the deuteration level is increased to 98% by about one degree.

Operating at a lower temperature, improves the damage threshold, reliability and reproducibility of the doubler with longer life of over 100 million shots. The disadvantage is that the angular acceptance ($L \times \Delta\theta$) is reduced to 30 cm-mr and the beam walk-off is 3 mrad. The angular acceptance is still six times greater than that for D-KDP (Type II) doubler. The spectral acceptance of D-CDA doubler is 22.5 cm-Å (FWHM) as compared to 55.7 cm-Å for D-KDP (Type II) doubler. Since angular acceptance is large in D-CDA doubler, focussing the beam is permissible with further improvement in the SHG efficiency.

The walk-off angle Ψ at room temperature (81° orientation angle) is given by

$$\Psi = \arctan\left[(n_{o1}/2)^2\{(n_{e2})^{-2} - (n_{o2})^{-2}\} \sin 2\theta\right]$$

= 3.1 mrad (room temperature, angle match)

= zero (90° phase match at 120°C)

The acceptance angle is given by (ℓ = 25 mm),

$$\alpha = \frac{\lambda}{2\ell}\left(\frac{1}{\Psi\,(n_{01})^2}\right)$$

= 2.6 cm-mrad (room temperature angle match)

= 30.0 cm-mrad (60°C phase match)

= 76.0 cm-mrad (90°C phase match at 120°C)

The walk-off angle of 3.1 mrad gives 80 micron deviation over a 25 mm long crystal. So the spot size w for 25 mm long crystal should be greater than 100 micron. For crystal D-KDP (type I angle 37°) the walk-off angle is 27 mrad and the acceptance angle 0.3 mrad so the spot size w is eight times greater than that for D-CDA crystal.

Applications of D-CDA:

Crystal D-CDA can be non-critically phase matched (NCPM) with Nd:YAG (1064 nm), Nd:Glass (1054 nm) and Nd:YLF (1047 nm). Typical dimensions of the different crystals available are summarized in Table IV.

TABLE IV

Crystal	Maximum cross-section	Maximum length
D-KDP	100 X 100 mm²	100 mm
D-CDA	50 X 50 mm²	40 mm
KTP	15 X 15 mm²	15 mm
BBO	10 X 10 mm²	15 mm
LBO	10 X 10 mm²	20 mm
$KNbO_3$	5 X 5 mm²	10 mm

D-CDA crystals offer the best choice for SHG of 1064nm, 1054nm and 1047nm at average powers approaching 50 watts producing efficiency in excess of 50%.

In one experiment with a pulse energy of 1 Joule/pulse at 20 Hz, 7 to 9 ns pulse width with beam diameter of 9.5 mm, over 55% SHG efficiency was achieved giving 10 watts of average power at 532 nm, with a 30 mm long crystal.

In a second experiment, I.4 Joules/pulse at 10 Hz produced over 50% efficiency. In 98% D-CDA crystals, over 25 watts of green is reported, for incident average powers of 50 watts. The average power handling capability of D-CDA is comparable to that of D-KDP.

Quantum Technology Inc. grows many crystals of non-linear materials and keeps a complete stock of crystals of KD*P, CD*A, KTP, LBO, BBO and $KNbO_3$. Ovens and temperature controllers are also available for phase matching temperatures up to 150°C. Please direct your inquiries at 407-333-9348.

TABLE V: COMPARISON OF NON-LINEAR OPTICAL PROPERTIES OF CRYSTALS.

	D-KDP	D-CDA	KTP	BBO	LBO	$KNbO_3$
Point group	$\bar{4}2m$	$\bar{4}2m$	mm2	3m	mm2	mm2
Refractive indices at 1064 nm	$n_o = 1.495$ $n_e = 1.455$	$n_o = 1.550$ $n_e = 1.533$	$n_{x=a} = 1.737$ $n_{y=b} = 1.740$ $n_{z=c} = 1.831$	$n_o = 1.655$ $n_e = 1.543$	$n_{x=a} = 1.566$ $n_{y=c} = 1.591$ $n_{z=b} = 1.606$	$n_x = 2.120$ $n_y = 2.220$ $n_z = 2.257$
Crystal Type	negative uniaxial	negative uniaxial	positive biaxial	negative uniaxial	negative biaxial	negative biaxial
Phase match angle at 1064 nm	37° Type I 53.5° Type II	81° Type I	21.9° Type II	22° Type I	11.79° Type I	57.2° Type I
Non-linear coefficients (pm/V)	$d_{36} = 0.63$	$d_{36} = 0.58$	$d_{32} = 5.0$ $d_{31} = 6.5$ $d_{33} = 13.7$ $d_{24} = 7.6$ $d_{15} = 6.1$	$d_{22} = 1.6$ $d_{31} = 0.08$	$d_{31} = 1.16$ $d_{32} = 1.24$ $d_{33} = 0.063$ $d_{15} = 1.15$ $d_{24} = 1.24$	$d_{31} = 15.8$ $d_{32} = 18.3$ $d_{33} = 27.4$ $d_{15} = 16.5$ $d_{24} = 17.1$
Transparency (microns)	0.22 - 1.1	0.26 - 1.1	0.35 - 4.4	0.19 - 2.5	0.16 - 2.6	0.42 - 4.2
Damage Threshold (MW/cm²)	350	350	150	2000	5000	350
SHG cut-off (nm)	740 Type II	1034 Type I	990 Type II	410 Type I	555 Type I	860 A cut 986 B cut
L. ΔT (cm– °C)	6.7	6	22	55	3.9	0.043
L. Δθ at CPM (cm-mrad)	5 Type II	30 Type I	15.7 Type II	0.523 Type I	31.3 Type I	11.9
$L^{1/2}$ Δθ ($cm^{1/2}$ - mrad)	N/A	76	N/A	1.5	71.9 NCPM at 148°C	38
L. Δλ (cm - Å)	55.7	22.5	4.5	6.6	N/A	0.6