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Applications of Non-Linear Crystals
Chapter in
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2.5.6 Nonlinear Optical Effects in Crystals

Nonlinear optics (NLO) is a powerful tool to generate coherent sources that may not be readily available through the lasing action in a medium. Many types of lasers are commercially available, offering a wide variety of different output wavelengths. However the number of different wavelengths available that are suitable for materials processing is somewhat limited.

For example, there are not many solid-state laser sources in the visible region, only the ruby laser operating at 649.3 nm. The Nd:YAG laser is one of the most well-developed industrial lasers, operating at 1064 nm in the near infrared region. The use of nonlinear-optical effects allows this laser wavelength to be halved, so as to generate coherent radiation at 532 nm (in the green). The 1064 nm wavelength can be further subdivided to produce one-third wavelength (355 nm) or one-fourth wavelength (266 nm) or to produce tunable visible coherent radiation. This wavelength shortening offers the advantage of reduced focal diameter, increased irradiance, and possibly higher absorption coefficient.

This section offers a brief introduction to nonlinear optics and also describes how nonlinear optics can be used to increase the range of possible laser wavelengths for materials processing.

The electric field, $\mathbf{E}(t)$, of electromagnetic radiation interacts with the electrical field within the molecules of a crystalline medium. It polarizes the atoms by slightly displacing the electrons along the direction of the field. At low intensities, the induced polarization, $\mathbf{P}(t)$, follows, with some phase retardation, the sinusoidal oscillation of a monochromatic wave. The temporal variation of the electric field is

$$\mathbf{E}(t) = \mathbf{E}_0 \sin(\omega t)$$

Maxwell's electromagnetic wave equations describe the linear-optical effects in the medium, and the response

$$\mathbf{P}(t) = e_0 \chi \mathbf{E}_0 \sin(\omega t + \Theta)$$

where e_0 denotes the electric permeability of vacuum, and χ and Θ are frequency-dependent material constants, referred to as the magnitude and phase of the electric susceptibility of the medium. This linear relationship between P and E generally fails to give an accurate description of the medium polarization for strong external electric fields $E >> 1$ kV/cm, such as those that are present in laser radiation. Lasers are the only radiation sources capable of producing sufficiently high electric fields to induce an appreciable nonlinear response in crystals.

Since its discovery by Peter Franken (1961) and his group, the field of nonlinear optics has established itself as an important research tool, benefiting several areas of science and technology. The most important practical implications of NLO arise from the possibility of converting coherent laser radiation to new frequencies. Thus frequency conversion in a suitable medium (dielectric solids or gases) allows researchers to develop coherent sources of wavelengths that are wanted, with a broad tuning range, and/or at frequencies where coherent laser sources are simply not available. For example, for underwater laser communication between two submarines, a coherent source at 532 nm (where water is most transparent) is required. This is achieved by frequency doubling an Nd:YAG laser operating at 1064 nm, in a crystal of potassium titanyl phosphate (KTP), or similar NLO medium.

For photon energies much smaller than the energy gap between populated and the lowest unpopulated excited states, the polarization response of these materials can be written as:

$$\mathbf{P}(t) = e_0\{\chi_1\mathbf{E}(t)^1 + \chi_2\mathbf{E}(t)^2 + \chi_3\mathbf{E}(t)^3 + \cdots\}$$

This expression is valid for weak nonlinearities, i.e., at moderate field strengths. The contributions to the induced polarization rapidly decrease with increasing order of nonlinear susceptibility χ_n ($n > 2$). The second-order term gives rise to second-harmonic generation (SHG), the third-order term gives rise to third-harmonic generation (THG), and so on.

Crystal Media for Nonlinear Optics

All piezoelectric crystals exhibit an electro-optic (EO) effect as well as a nonlinear optical (NLO) effect. A good NLO crystal must be anisotropic, that is, the properties depend upon the direction of propagation in the crystal. Whether a crystal is isotropic or anisotropic, and in the latter case, whether it is uniaxial (one optic axis) or biaxial, is determined by the crystal symmetry. Thus crystals with a cubic symmetry are always isotropic. All others are anisotropic. Crystals with trigonal, tetragonal, and hexagonal symmetries are always uniaxial; and crystals with orthorhombic, monoclinic, and triclinic symmetries are always biaxial. For an NLO crystal device to work well without degradation of performance over the lifetime of its assignment, it must meet a number of criteria.

1. Reliable crystal growth techniques for adequate size
2. NLO susceptibility coefficient
3. Birefringence (n_o - n_e) and optical dispersion
4. Moderate to high transparency
5. Good optical homogeneity
6. Good mechanical strength
7. Chemical stability
8. Ease of polishing and antireflection coating
9. Low linear and nonlinear absorption
10. Temperature phase-matching bandwidth
11. Fracture toughness
12. Damage threshold
13. Nonlinear index of refraction
14. Brittleness

Recent efforts in molecular engineering are making progress in growing crystals such as barium borate (BBO), lithium borate (LBO), and cesium-lithium borate (CLBO).

The terms that are often used in connection with NLO work are:

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1. *Ordinary ray (O ray)*—optical ray that obeys Snell's law.

2. *Extraordinary ray (E ray)*—ray that does not obey Snell's law. The phase velocity of this ray depends upon the direction of polarization.

3. *Birefringence*—the double refraction in a crystal forms an E-ray and an O-ray, and its value is $(n_o - n_e)$.

4. *Beam walkoff*—the angular deviation between the O-ray and the E-ray as they propagate through the crystal. Along the optic axis, it is zero as the two rays propagate with equal velocity and $n_o = n_e$.

5. *Phase-matching (PM) condition*—expressed by the law of conservation of momentum, and given by $K_{\omega_1} + K_{\omega_2} = K_{\omega_3}$.

6. *Second-harmonic generation (SHG),* also called frequency doubling—a special case of mixing of two waves of the same frequency (ω_1) to obtain a wave of double the frequency ($\omega_2 = 2\omega_1$) or half the wavelength.

Other terms similar to this are sum frequency mixing (SFM) and difference frequency mixing (DFM), used for mixing of two waves of different frequencies ($\omega_1 + \omega_2 = \omega_3$) or subtracting these two waves ($\omega_1 - \omega_2 = \omega_3$) to generate a third frequency. The SHG or SFM process combines two low-energy photons into a high-energy photon of the third frequency, at a lower wavelength (downconversion). In the case of DFM, one low-energy photon is taken away from a high-energy photon to generate a third low-energy photon in the infrared (upconversion).

In the case of SFM, the final wavelength, governed by the law of conservation of energy, is given by the equation:

$$\frac{1}{\lambda_1} + \frac{1}{\lambda_2} = \frac{1}{\lambda_3}$$

The PM angle condition that must be satisfied is given by the equation:

$$\frac{n_{\omega_1}}{\lambda_1} + \frac{n_{\omega_2}}{\lambda_2} = \frac{n_{\omega_3}}{\lambda_3}$$

DFM is expressed by a similar equation.

7. *Critical phase matching (CPM)*—in SHG, the NLO process is most efficient when the ω_1 and ω_2 phase velocities are made equal by choosing the internal crystal angle between the input plane of polarization and the optic axis of the crystal. This is called critical phase matching or sometimes angle phase matching or angle tuning (AT). Both conservation of energy and conservation of momentum must be satisfied.

8. *Noncritical phase matching (NCPM)*—when this angle is set at 90°, it may be possible to make ΔK [given by $K_{\omega_3} - (K_{\omega_1} + K_{\omega_2})$] vanish in some crystals by taking advantage of their thermal birefringence. When ω_1 propagates normal to the optic axis, the output beam ω_2 is also normal to it and all the rays (inside and outside the crystal) are collinear (zero beam walkoff). This is called noncritical phase matching or sometimes temperature tuning (TT). This is preferred because it produces the highest efficiency possible from the NLO material.

9. *Type I phase matching process*—cases (7) and (8) fall in this category, where the input plane of polarization is perpendicular to the plane containing the optic axis. This is also called an oo-e interaction for a negative ($n_e < n_o$) uniaxial crystal, or an ee-o interaction for a positive crystal (see Fig. 16A).

10. *Type II phase matching*—it is also possible to angle phase match when the plane containing the optic axis is rotated by 45°, so that two rays (one an E ray and the other an O ray) enter the crystal and the third (mixed) frequency ray is an E ray. This is called an eo-e interaction. Type II angles usually need numerical calculations. For biaxial crystals, such as KTP, LBO, or $KNbO_3$ (potassium niobate), these calculations are quite involved (see Fig. 16B).

11. *Optical parametric oscillation (OPO)*—an NLO process where the crystal is placed in a resonator and pumped by high-energy radiation (ω_3) to generate two frequencies called signal (ω_1) and idler (ω_2). A high-energy photon is split into two low-energy photons and in a degenerate case, by choice of a proper angle, $\omega_1 = \omega_2$, and the output frequency is one-half the input frequency; thus the wavelength is doubled by this process (see Fig. 17A).

12. *Intracavity frequency doubling*—an NLO crystal is placed inside the laser cavity, where the circulating powers are high, to obtain high efficiency in a CW laser (see Fig. 17B).

13. *Angular acceptance width*—the angular radiation that can be accepted by the crystal. Similar terms are spectral acceptance width and temperature acceptance width, and each NLO crystal has a unique property.

14. *Figure of merit*—the ratio d^2/n^3, where d is the nonlinear susceptibility coefficient and n is the refractive index. The converted SHG output is higher when this figure is larger.

15. *Efficiency of conversion*—in the case of SHG, it is the ratio of power at ω_2 to that at ω_1.

16. *Damage threshold*—a property of the crystal to withstand the laser radiation without damage.

17. *Deuterated crystal*—crystal such as KDP (potassium dihydrogen phosphate) grown in deuterium oxide (heavy water) and called D-KDP or KD*P, (deuterated KDP or potassium dideuterium phosphate).

18. *Coherence length*— that length over which the two waves (ω_1 and ω_2) remain in a constant phase relationship.

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Most important selection rules for the NLO crystal are:

1. High NLO coefficient and large figure of merit.
2. Phase matchability and excellent transmission over the region of interest.
3. Large angular, spectral, and temperature acceptance widths.
4. Large damage threshold.
5. Large size with optical homogeneity.

For example, KDP crystal frequency doublers, grown for laser fusion, are 750x750 mm^2 in cross section with a length of 500 mm, while the largest KTP, BBO, or LBO crystal size is about 15 x 15 x 20 mm^3. KDP-type crystals are grown near room temperature, while BBO type crystals are grown at about 900°C.

Second Harmonic Generation

The simplest case of NLO mixing is that of SHG. The second-harmonic (SH) power generated by a single mode, Gaussian beam of angular frequency ω_1, and power P incident along the principal axis of a plane parallel crystal rod of length L is given by

$$P_{\omega_2} = \frac{J(P_{\omega_1})^2 L^2 d^2 \sin^2 \Theta}{W_0} \left(\frac{\sin^2 x}{x^2} \right)$$

where $x = \Delta KL / 2$

and the efficiency of conversion is given by the ratio $P\omega_2 / P\omega_1$. Here J is a crystal dielectric constant at ω_1, d is the effective

Table 7. Parameters and Typical Performance of Some Nonlinear Crystals

Material	Refractive index			Nonlinear susceptibility		Nominal damage threshold		Linear absorption	Temperature acceptance	Angular acceptance	Length used	Typical SHG efficiency
	λ (nm)	n_o	n_e	$d \times 10^{12}$ d_{14}	m/volt d_{36}	t_p (ns)	(GW/cm^2)	(% per cm)	$\Delta T \cdot d$ (°C cm)	$\psi \cdot d$ (mrad cm)	(cm)	(%)
ADP	347	1.55	1.50						0.8	32.0	6.0	23
	530	1.53	1.48									
	694	1.52	1.48	0.48	0.49			3%				
	1060	1.51	1.47	0.55	0.56	60.0	0.5					
KDP	347	1.54	1.49						3.5	1.0	2.5	20
	530	1.51	1.47			0.2	17.0					
	694	1.51	1.47	0.47	0.47	20.0	0.4	2.4%				
	1060	1.49	1.46	0.49	0.47	0.2	23.0	3%				
KD*P	347	1.53	1.49						6.7	1.7	3.8	25
	530	1.51	1.47					0.6%				
	694	1.50	1.46	0.46	0.50							
	1060	1.49	1.46	0.50	0.50	10.0	0.5	0.6%				
RDP	347	1.53	1.50					1.5%			2.0	20
	530	1.51	1.48									
	694	1.50	1.47			10.0	0.2	1%				
	1060	1.50	1.47	0.56	0.48	12.0	0.3	4%				
RDA	347	1.60	1.55					5%	3.3	40.0	2.0	25
	694	1.55	1.50		0.42	10.0	0.35	3.5%				
CDA	347	1.60	1.57						5.8	70.0	3.0	22
	530	1.57	1.55									
	694	1.56	1.54									
	1060	1.55	1.53		0.43	10.0	0.5	4%				
CD*A	347	1.59	1.57						6.0	70.0	3.0	30
	530	1.57	1.55					0.4%				
	694	1.56	1.54									
	1060	1.55	1.53		0.43	12.0	0.36	0.6%				

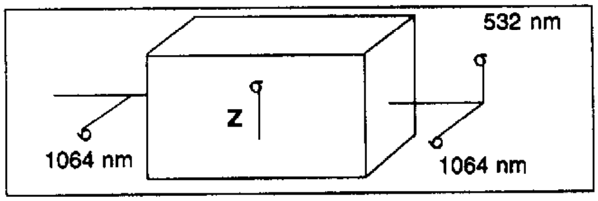

Figure 16A. Type I noncritically phase-matched (NCPM) crystal D-CDA (deuterated cesium dihydrogen arsenate) for efficiently doubling of 1064 nm radiation to 532 nm, with temperature tuning at 110ºC.

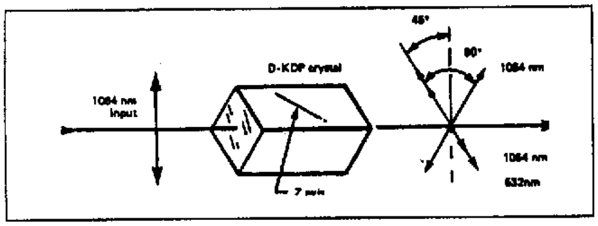

Figure 16B. Type II angle-phase-matched (angle tuned) crystal D-KDP for doubling 1064 nm radiation to 532 nm.

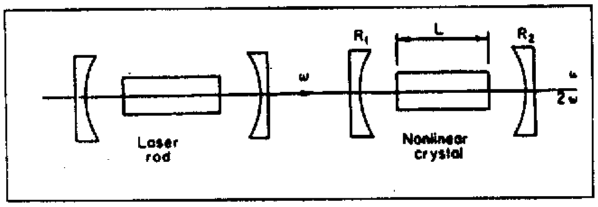

Figure 17A. Optical parametric oscillator (OPO) where a proper NCPM or CPM crystal is employed in a resonator with specially coated (reflective) mirrors. For an NLO application, a large number of parameters of the laser as well as those of the crystal must be taken into account. Also, tuning a crystal requires special skills and equipment, mounts, and a great deal of attention to detail to obtain fruitful results, unlike tuning a station on the radio dial. A number of questions need to be answered to succeed in the experiment.

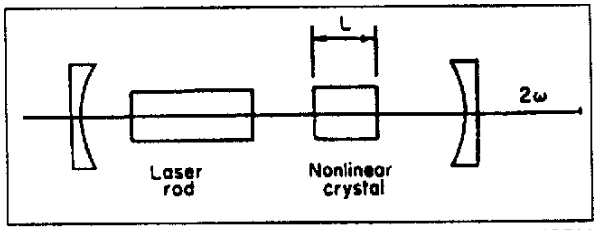

Figure 17B. Intracavity SHG where an NLO crystal, either NCPM or CPM Type I or Type II, is employed.

SHG coefficient depending upon the NLO susceptibility, W_0 is the minimum beam waist, and Θ is the angle between the crystal optic axis and the plane of polarization of ω_1. Because of dispersion, there is usually a wave vector mismatch ΔK between ω_1 and ω_2. For a fixed ΔK, the function $\sin^2 x/x^2$ undergoes oscillation as a function of crystal length with a period $2\pi/x$. Half this distance is called the coherence length and is the distance from the input at which the SH power is a maximum. Typical values range from a few millimeters to several centimeters. For normal incidence, the coherence length is given by $L_{coh} = \lambda_1 / 4 (n_{\omega_2} - n_{\omega_1})$, where λ_1 is the fundamental wavelength.

Phase-Matching Angles

The phase-matching angles for Type I (Θ_1) and Type II (Θ_2) can be calculated. For negative uniaxial NLO crystals, such as KD*P, CD*A, BBO, or $LiIO_3$ these are given by
Type I PM angle:

$$\sin^2\Theta_1 = \{ [n_{0\omega_1}]^{-2} - [n_{0\omega_2}]^{-2} \} / \{ [n_{e\omega_2}]^{-2} - [n_{o\omega_2}]^{-2} \}$$

Type II PM angle:

$$\left[\frac{\cos^2\Theta_2}{\left(n_{o\omega_2}\right)^2}+\frac{\sin^2\Theta_2}{\left(n_{e\omega_2}\right)^2}\right]^{-1/2}=\frac{1}{2}\left[\left(n_{o\omega_1}\right)+\left\{\frac{\cos^2\Theta_2}{\left(n_{o\omega_1}\right)^2}+\frac{\sin^2\Theta_2}{\left(n_{e\omega_1}\right)^2}\right\}^{-1/2}\right]$$

Inorganic NLO Materials

Visible and New Infrared Materials: Crystals of the KDP family have a transmission range from 220 to 840 nm (90% inclusive of Fresnel losses). These crystals are fairly easy to grow in a crystallizer by dropping the temperature of a solution of KDP salt in water. For materials grown in heavy water, transmission is from 220 to 1240 nm. There are seven members, KDP, ADP (ammonium dihydrogen phosphate), RDP (rubidium dihidrogen phosphate), ADA (ammonium dihydrogen arsenate), KDA (potassium dihydrogen arsenate), RDA (rubidium dihydrogen arsenate), CDA, and seven other deuterated isomorphs, KD*P, AD*P, RD*P, AD*A, KD*A, RD*A, and CD*A. The chemical formula for KDP is KH_2PO_4 and that for KD*P is KD_2PO_4. In the case of ADA, it is $NH_4H_2AsO_4$. These crystals are commonly used as they have broad angle of tunability; a ± 5° angle change tunes the wavelength from 600 to 800 nm in Type I KDP. When a crystal KDP is angle phase matched, that is, oriented at the proper PM angle, a 30-mm-long rod can produce SHG efficiency of 10 to 20% with a dye laser, since the d_{eff} coefficient is small. These crystals have similar values of nonlinearity within 20% of each other, and therefore these produce about the same efficiency under similar conditions. Crystal ADP angle phase matched at 600 nm (angle 61.5°) will produce slightly better results than a crystal KDP angle phase matched at 600 nm (angle 60°). However, if it is possible to find an NCPM crystal at 600 nm, higher efficiencies up to 30% are achievable. Fortunately, crystal ADA can be temperature tuned (NCPM) at 68°C for SHG at 600 nm.

Table 7 shows typical performance and parameters of some of these crystals.

Figure 18 shows the Type I angles for phase matching for some of these crystals as well as for $LiIO_3$ (hexagonal, 320 to 3800 nm), BBO (trigonal, 200 to 2000 nm), and LBO (orthorhombic, 200 to 2200 nm) crystals.

The important feature is that these crystals operate in an NCPM mode over a narrow range; for example, crystal ADA will produce excellent SHG efficiency (without beam walkoff) from 585

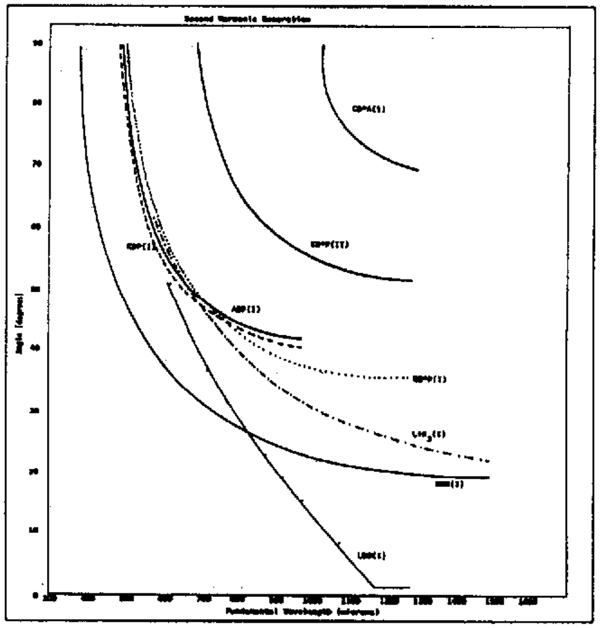

Figure 18. Tuning angles versus wavelengths for selected crystals.

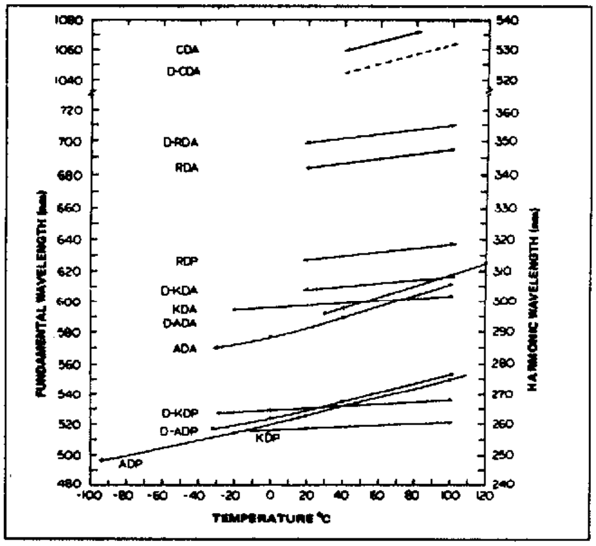

Figure 19. Temperatures for NCPM versus wavelength for KDP materials.

to 620 nm over the temperature range +25 to +125°C. For a rod length of 30 mm, the SHG efficiency is about 20–40%. Crystal RDA is an NCPM doubler for ruby (PM temperature of 92°C) and CD*A is an NCPM doubler for Nd:YAG (PM temperature of 110°C). The efficiency of RDA is 30–40% and that of CD*A is 50–60%. The peak power damage threshold of these crystals is about 250 MW/cm^2. The fluence damage threshold is 10 J/cm^2.

For NCPM crystals, the angular acceptance is large; so it is customary to use a 50-cm focal length lens and to place the crystal halfway between the lens and the focus. To increase the power density, a beam reducer is sometimes employed. If the power density is too high, a beam expander is required. Since these are hygroscopic materials, the crystal rods must be protected with antireflection (AR) coated windows in a hermetically sealed housing. The maximum safe operating temperature for NCPM is about 120°C. These crystals need special care in handling (use of gloves), storing, polishing, and AR coating, because they can crack from thermal shock (rate of temperature rise > 5° / min).

BBO and LBO crystals are excellent harmonic generators for Nd:YAG, Ti:Sapphire, and alexandrite lasers because of their high damage threshold and ultraviolet transmission. With a BBO rod 7 mm in length, cut at an angle 31° (Type 1), 32% conversion efficiency is achieved in the ultraviolet (378 nm). With a high-average-power (100 W) Nd:YAG laser (100 mJ, 14 ns, 1000 Hz), 37% efficiency is obtained (extracavity) without thermal detuning. Crystal LBO, operated (NCPM) intracavity, produces 50% SHG efficiency in a diode-pumped Nd:YAG (100 W) laser. Figure 19 shows the NCPM temperatures for various wavelengths for KDP-type crystals. Figure 20 shows the Type II phase-matching angles for various wavelengths for KDP, BBO, and LBO crystals.

Mid-Infrared Materials: There are many crystals that are useful in the mid-IR range from 2 to 5 μm. These crystals are

1. Lithium niobate, $LiNbO_3$ (trigonal, 420 to 4500 nm)
2. Potassium niobate, $KNbO_3$ (orthorhombic, 450 to 5000 nm)
3. Barium sodium niobate, $Ba_2Na(NbO_3)_5$, also known as banana (orthorhombic, 460 to 5000 nm)
4. Potassium titanyl phosphate, KTP (orthorhombic, 420 to 4500 nm).

Banana is now replaced for SHG at 1064 nm by KTP, or MgO-doped lithium niobate (LN). MgO-doped (5%) LN has a higher damage threshold.

There are many homologs of KTP available, such as KTA, RTA, and CTA. These have similar properties with slight variations. While LBO and BBO are grown by the flux method at temperatures around 1000°C, niobates are grown by the Czochralski method at 1400°C. KTP crystals are grown by either the flux method or the hydrothermal method. All crystals grown by the flux method tend to have inclusions and defects that lower the damage threshold. BBO and LBO are hygroscopic and suffer from degradation of polished faces.

Table 8. Properties of Nonlinear Optical Materials, Part A

Unixial crystals	KD*P	ADP	CD*A		BaB_2O_4		$LiNbO_3$		$LiIO_3$
Refractive index									
n_o	1.4931	1.5087	1.5500		1.6551		2.2322		1.8567
n_e	1.4582	1.4680	1.5431		1.5425		2.1560		1.7168
Transparency (µm)	0.18–1.8	0.184–1.5	0.27–1.66		0.198–2.6		0.35–5		0.31–5 ;*c* 0.34–4 $\perp c$
Nonlinear susceptibility (pm/V)									
$d_{21}=d_{16}$	0	0	0		-2.3		-2.1		0
d_{22}	0	0	0		2.3		2.1		0
$d_{14}=d_{25}=d_{36}$	0.37	0.47	0.3		0		0		(0)
$d_{31}=d_{15}$	0	0	0		0.1		-4.3		4.4
$d_{32}=d_{24}$	0	0	0		0.1		-4.3		4.4
d_{33}	0	0	0		0		-27		4.5
Thermo-optic coefficient (10^{-6} K^{-1})									
dn_o/dt	-30	-52	-25		-17		5		-89
dn_e/dt	-20	0	-16		-9		38		-75
Noncritical wavelength (µm) Type 1	0.519	0.524	1.045		0.409		1.062		0.378
Thermal Conductivity (W/m K)									
k_{11}	1.86	1.26	(1.5)		0.08		(5.6)		(1.47)
k_{33}	2.09	0.71	—		0.8		—		
Phase matching			T_{pm}= 112°				T_{pm}= 107°		
Type	II	II	I	I	I	II	I	I	I
θ	54	62	82	90	23	32	77	90	30
ϕ	—	—	—	—	—	—	—	—	—
Nonlinear susceptibility									
d_{eff} (pm/V)	0.35	0.39	0.30	0.30	1.9	1.6	5.1	4.7	1.8
C^2 (GW^{-1})	1.0	1.2	0.62	-0.63	22	16	70	59	13
Angular acceptance									
(mrad cm) critical									
(mrad cm) noncritical	2.3	2.2	7.2	51	0.53	0.80	1.2	33	0.34
Walkoff angle									
ρ_ω (deg)	1.3	1.2	0	0	0	3.8	0	0	0
$\rho_{2\omega}$ (deg)	1.4	1.5	0.26	0	3.2	3.9	1.0	0	4.3
Temperature bandwidth (°K cm)	12	2.1	3	3.3	51	37	1.0	0.75	23
Wavelength bandwidth (nm cm)	5.6	26	2.5	2.5	2	2.1	0.31	0.31	0.82
Threshold power P_{th} (MW)	30	27	3	NA	21	13	0.70	NA	66
Resonant SHG P_{50} (W)	120	210	46	26	3.6	5.8	0.38	0.05	6.6
Maximum drive C^2I_{dam} (cm^{-2})	5(1 ns)	7(15 ns)	0.15	0.16	297	216	700	590	26 (1 ns)
			(12 ns)		(1 ns)				
Thermal dephasing η/δ_{th}	5×10^{-4}	8×10^{-6}	5×10^{-4} - 7.4×10^{-4}		0.01×10^{-3} - 4×10^{-3}		0.1	0.4	0.05
Thermal focusing f_{th} (cm W)	-3.9	-0.13	-6.8		-3.8		47		-12
Surface damage intensity (GW/cm²)	5(1 ns) >8(0.6 ns, 0.53 µm)	6(15 ns) >8(0.6 ns, 0.53 µm)	0.25(12 ns)		13.5(1 ns) 23(14 ns) 32(8 ns, 053 µm)		10(1 ns) 0.3(10 ns)		2(1 ns) 1(0.1 ns, >0.53 µm)

$AgGaS_2$	$AgGaSe_2$	$ZnGeP_2$
2.3472	2.5912	3.0728
2.2934	2.5579	3.1127
0.5–13	0.78–18	0.74–12
0	0	0
0	0	0
@17.5	33	69
(11.2 10.6 μm)	(10.6 μm)	(10.6 μm)
0	0	0
0	0	0
0	0	0
154 (10.6 μm)	70 (3.39 μm)	150
155 (10.6 μm)	40 (3.39 μm)	170
1.8, 11.2	3.1 , 12.8	3.2 , 10.3
(11.5)	(1)	(35)
I	I	I
31	52	56
—	—	—
10.4	28	70
14	81	292
3.7	6.0	5.0
0	0	0.65
1.2	0.64	0
50	50	40
11	22	20
4.3	0.25	0.069
6.9	0.58	0.68
0.4 (10 ns)	3 (10 ns)	15 (25 ns)
0.15	0.14	13
13	1.5	1.0
0.025(10 ns) 0.5(10 ns, bulk)	0.01 0.04 (50 ns, 2 μm) 0.02 0.03 (10 ns, 10.6 μm)	0.05(25 ns, 2 μm) 1(2 ns, 10.6 μm)

Table 8. Properties of Nonlinear Optical Materials, Part B

Bixial crystals	**KTP**	**$KNbO_3$**	**LiB_3O_5**
Refractive index			
n_x	1.7367	2.1194	1.5649
n_y	1.7395	2.2195	1.5907
n_z	1.8305	2.2576	1.6052
Transparency (μm)	0.35–4.5	0.4–5.5	0.16–2.3
Nonlinear susceptibility (pm/V)			
$d_{21} = d_{16}$	0	0	0
d_{22}	0	0	0
$d_{14} = d_{25} = d_{36}$	0	0	0
$d_{31} = d_{15}$	2.0	-11.3	-0.67
$d_{32} = d_{24}$	3.6	-12.8	0.85
d_{33}	8.3	-19.5	0.04
Thermo-optic coefficient (10^{-6} K^{-1})			
dn_x/dt	11	60	-1.9
dn_y/dt	13	22	-13
dn_z/dt	16	-35	-8.3
Noncritical wavelength (μm)			
Type I	—	0.860	0.554
		0.982	1.212
Type II	0.990	—	1.19
	1.081		
Thermal conductivity (W/m K)			
k_{11}	2	—	(3)
k_{22}	3	(5.6)	—
k_{33}	3.3		—
Phase matching			
type		T_{pm} = 183°	T_{pm} = 148°
	II	I I	II I
θ	90	71 90	70.1 90
ϕ	23	90 90	90 0
Nonlinear susceptibility			
d_{eff} (pm/V)	3.2	-11 -13	0.69 0.85
C^2 (GW^{-1})	47	312 390	3.2 4.6
Angular acceptance (mrad cm)			
critical			
noncritical	9	0.24 13	9.4 72
Walkoff angle			
ρ_ω (deg)	0.20	0 0	0.33 0
$\rho_{2\omega}$ (deg)	0.27	2.5 0	0 0
Temperature bandwidth (K cm)	17	0.5 0.3	6.2 3.9
Wavelength bandwidth (nm cm)	0.46	0.12	4.6 3.6
Threshold power P_{th} (MW)	0.029	4.0 NA	1.7 NA
Resonant SHG P_{50}(W)	0.28	0.24 0.01	17 8.6
Maximum drive $C^2 I_{dam}$ (cm^{-2})	470 (1 ns)	2200 2730 (1 ns)	4.5 6.4 (12 ns)
Thermal dephasing η/δ_{th}	0.9	0.07 0.6	0.1 0.2
Thermal focusing f_{th} (cm W)	36	22	-440
Surface damage intensity (GW/cm^2)	9-20 (1ns)	7 (ns)	25 (0.1 ns)

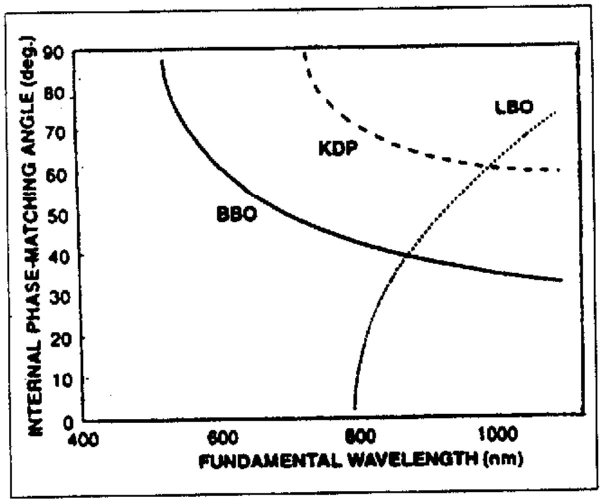

Figure 20. Type II PM angles versus wavelength for several nonlinear crystals.

Both materials are difficult to AR coat. Niobates and KTP are easy to AR coat, and their polish does not degrade. Crystal lithium iodate (LI), (hexagonal, 320 to 3800 nm) is also usable in the midinfrared range. It is grown by dropping the temperature of the solution of the salt in water and the crystal polished faces degrade with time even at low relative humidity. It is, however, easy to AR coat with magnesium fluoride.

Far-Infrared Materials: There are three popular materials:

1. Crystal silver gallium sulfide, $AgGaS_2$ (tetragonal, 500 to 13,000 nm)
2. Silver gallium selenide, $AgGaSe_2$ (tetragonal, 780 to 18,000 nm)
3. Zinc germanium phosphide, $ZnGeP_2$ (tetragonal, 740 to 12,000 nm).

Their NLO properties, as well as those of other materials, useful in the near and mid-IR are given in Table 8. All data are for room temperature and 1.06 μm, unless otherwise noted.

For frequency conversion of a CO_2 laser, a few other crystals besides the three mentioned in Table 8 are available. These are crystals of proustite ($AgAsS_3$) and TAS (Tl_3AsSe_3). Conversion efficiency of 40% is achievable in crystal TAS at 10 MW/cm^2 and of 60% is achievable in silver gallium selenide at 12 MW/cm^2. Both crystals have low absorption, high damage threshold, and moderate d_{eff}. The selenide is limited by the surface damage threshold, although the bulk damage is higher by one order of magnitude. These crystals are used in an OPO pumped by a Nd:YAG laser (1340 nm) or by Ho:YAG (2050 nm). These crystals can produce frequency doubling of 4000 nm radiation.

Third Harmonic Generation (THG) and Sum Frequency Mixing (SFM)

For a Ti:Sapphire laser, LBO Type I (31.8° at 800 nm) is used as a doubler and BBO type II (55.2°) is used as a tripler to generate 266 nm. The residual 800-nm radiation coming out of a doubler is mixed with 400-nm radiation in a tripler. The tripler can be a Type I crystal (44.3° angle); however, a wave plate is needed to rotate the plane of polarization of the 800-nm radiation to coincide with that of the 400 nm. This process is also called sum frequency mixing (SFM, mixing of 800 and 400 nm). SFM of two dye lasers has generated 197-nm radiation in a BBO crystal. Similarly it is possible to generate fourth-harmonic (quadruple, 266 nm), as well as fifth-harmonic (quintuple, 212.8 nm) radiation from a Nd:YAG laser in a BBO crystal (by mixing the fourth harmonic with the fundamental [4 + 1] radiation). The only crystal phase matchable for fifth-harmonic generation is BBO. It is difficult to generate ultraviolet below 200 nm because good optical-quality NLO crystals are not yet available.

Since BBO and LBO crystals are expensive in large sizes, a popular method of Nd:YAG laser tripling is to use Type I NCPM CD*A as a doubler and Type II KD*P as a tripler.

Optical Parametric Oscillator (OPO)

The OPO process is an NLO process in which a high-energy pump photon (ω_3) propagating in an NLO crystal spontaneously breaks down into two low-energy photons ($\omega_1 + \omega_2$) with the total photon energy conserved (i.e., $\omega_3 = \omega_1 + \omega_2$). The gain mechanism is based upon the stimulation emission process. The rate of emission through the NLO parametric process is proportional to the photons present. OPO is an inverse process of SFM. An NLO crystal is placed in a cavity formed by two mirrors. For a fixed pump wavelength, many signal and idler wavelengths

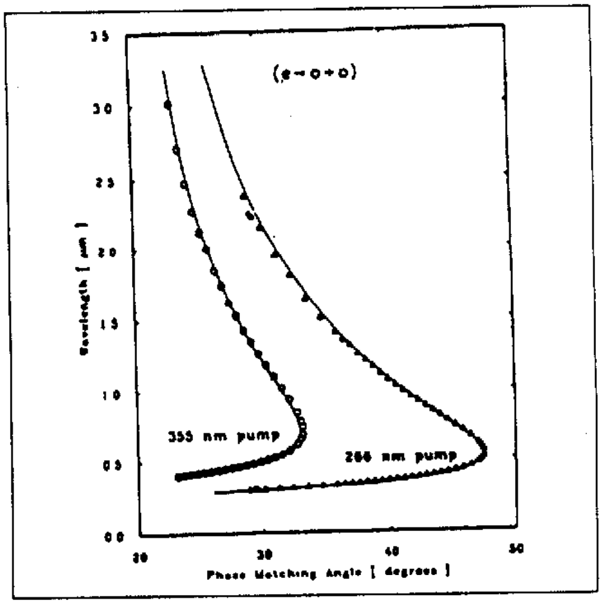

Figure 21. Tuning curves for an OPO based on BBO.

can be generated by tilting an NLO crystal. BBO, KTP, LBO, and $AgGaSe_2$ are good NLO crystals for achieving efficiencies greater than 30–40%.

Figure 21 shows tuning curves for Type I, 355 nm pumped BBO OPO.

Figure 22 below shows a typical experimental setup.

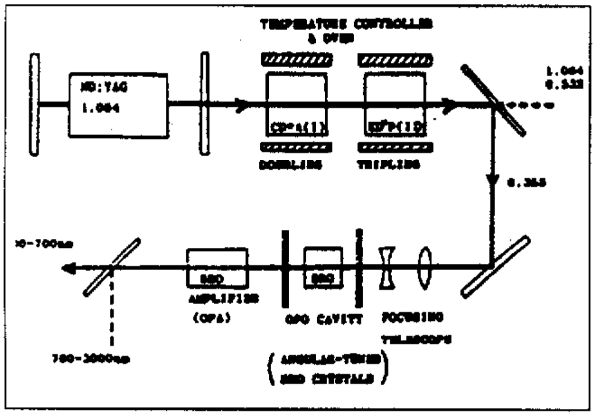

Figure 22. Typical arrangement for an OPO.

Wavelengths for Materials Processing

Materials processing is the broad field of cutting, drilling, welding, and otherwise modifying industrial materials and includes both metals and nonmetals. CO_2 and Nd:YAG lasers are by far the most widely used. Both CW and pulsed lasers are used, depending upon the application. Recently, solid-state diode lasers (emitting 809 nm radiation) have been used to pump Nd:YAG rods at the absorption peak. This improves the optical pump efficiency of Nd:YAG lasers as compared to the krypton lamp pumped lasers. For example, to achieve 50 W 1064 nm output, the electrical power to the diode lasers is about 240 W, whereas for the same output, a flash lamp consumes about 19 times more power. This new advancement has made Nd:YAG lasers more attractive than CO_2 lasers.

During the laser processing of materials, the conversion of the laser radiation into material removal can be significantly more efficient in the visible and ultraviolet regions than in the infrared. For this, 532, 355, and 266 nm are generated using NLO methods in a Nd:YAG laser. In a CW acousto-optically Q-switched Nd:YAG laser, a NCPM LBO crystal is used at a temperature of 149°C, and 50 W of green (multimode) or 8 W of TEM_{00} mode is available in a standard commercial laser. Crystal LBO is seven times more damage resistant than crystal KTP. Two other crystals, MgO-doped lithium liobate and potassium niobate, will generate 532 nm at NCPM temperatures of 107 and 200°C, respectively. However, these also have lower damage thresholds.

Third-harmonic 355 nm can be produced by using Type I LBO (in place of CD*A) and Type II LBO (in place of KD*P). Again 266 nm is produced in LBO (Type I) by mixing (3 + 1) or in crystal BBO (Type I) by doubling 532-nm radiation. There are advantages of reliability in using an all-solid-state system (as compared to excimer lasers). One can obtain with average powers up to 1 W in the ultraviolet for semiconductor and microelectronics manufacturing industries.

A harmonic frequency conversion flow chart for generating many typical wavelengths is shown in Figure 23.

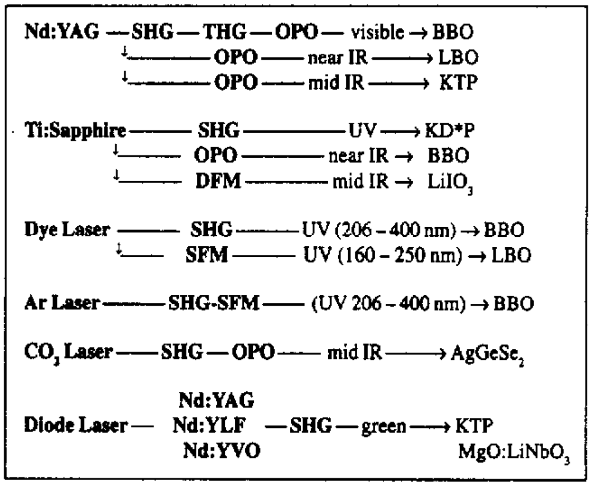

Figure 23. Harmonic frequency generation flow chart.

In an NLO system design, there are many variables that must be considered to optimize the efficiency. NLO crystals play an essential role for the generation of coherent sources in spectral ranges where useful levels of direct output from existing lasers cannot be achieved for materials processing applications.

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