Nonlinear Optics & Materials

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“Nonlinear optics” is the study of the interaction of intnse laser light with matter, which modifies its optical properties. These processes are almost magical, as they permit light of one colour (wavelength) to be converted into the light of a different colour. Typically, only laser light is sufficiently intense to modify the optical properties of a material system. The beginning of the field of nonlinear optics is often taken to be the discovery of second-harmonic generation by Franken et al. (1961), shortly after the demonstration of the first working laser by Maiman in 1960.

In the case of conventional (linear) optics, where the field strength is small, the electric polarization vector ***P*** is linearly proportional to the electric field strength ***E*** of an applied optical wave, i.e.

 (1)

Where *ε0* is the free-space permittivity, *χ* is the susceptibility of a given medium and a plot of ***P*** versus ***E*** is a straight line. The quantity is a constant only in the sense of being independent of ***E***; its magnitude is a function of the frequency. With sufficiently intense laser radiation this relation does not hold good and has to be generalized to equation (2), which can be written in the vector form, as by a power series

 ***P***(t) = *ε0*[*χ(1)* ***E***+ *χ(2)****E***2 +*χ(3****) E***3 + --------]

 = (2)

The quantities *χ(2)* and *χ(3)* are known as the second- and third-order nonlinear optical susceptibilities, respectively. For vector nature of field *χ(1)* is a second-rank (linear) tensor, *χ(2)* is a third-rank (nonlinear) tensor, and *χ(3)* is a forth-rank (nonlinear) tensor and so on. The values of the tensor coefficients are functions of frequency and temperature and the polarization, depends on *t* only on the instantaneous value of the electric field strength. The assumption that the medium responds instantaneously also implies that the medium must be lossless and dispersionless. The second-order nonlinear optical interactions can occur only in noncentrosymmetric crystals, i.e, in crystals that do not display inversion symmetry. Since liquids, gases, amorphous solids (such as glass), and even many crystals display inversion symmetry, *χ(2)* vanishes identically for such media, and consequently such materials cannot produce second-order nonlinear optical interactions. On the other hand, third-order nonlinear optical interactions (i.e. those described by a *χ(3)* susceptibility) can occur for both centrocymmetric and noncentrosymmetric media.

In equation (2) the term *χ(2)****E*2** is responsible for all of the two-wave effects. This includes second harmonic generation (SHG) (two fields at *ω* to make one at 2*ω*) and optical parametric oscillation (OPO) (one field at *ω*1 and other field at *ω2* to create fields at *ω1 - ω2* and *ω1 + ω2*). This also includes optical mixing, and the Pocals effect (change of index of refraction with applied electric field). The nonlinear polarization tensor  vanishes in the crystals that have a center of symmetry (i.e. crystal symmetry). In these crystals second harmonic generation is not possible. As a result of, many of the components of will be zero or equal to other components of the tensor. Thus the second-order polarization and the corresponding monochromatic components of the optical field:

  (3)

wheredenotes the second-order susceptibility that is a third-order tensor. The term *χ(3****) E*3** is responsible for all of the three wave effects. This includes third harmonic generation (three fields at *ω* to make one at 3*ω*) and various combinations of three fields to produce sum and difference frequencies as in four-wave mixing. This also includes the Kerr effect (where the index of refraction is a function of the input light intensity). The imaginary component of *χ(3)* is responsible for Raman, Brillouin, and Rayleigh scattering, as well as for two-photon absorption.

In the present chapter we shall discuss light propagation through crystals in the presence of an externally applied electric field. This field can in general, alter the refractive indices of the crystal and thus could induces birefringence in isotropic crystal, or could alter the birefringence property of the crystal. This effect is known as the electrooptic effect. If the changes in the refractive indices are proportional to the applied electric field, such an effect is known as Pockel’s effect or the linear electro-optic effect. If the changes in indices are proportional to the square of the applied electric field, the effect is referred to as the quadratic electrooptic effect or the Kerr effect.

1. **Second-Harmonic Generation (SHG)**

 As an example of a nonlinear optical interaction, let us consider the process of second-harmonic generation, which is illustrated schematically in Fig. 1. Here a laser beam whose electric field strength is represented as

 (4)

 is incident upon a crystal for which the second-order susceptibility is nonzero, The second-order nonlinear polarization that is created in such a crystal is given according to Eq. (3) as or explicitly as

 (5)

We see that the second-order polarization consists of a contribution at zero frequency (the first term) and a contribution at frequency 2*ω* (the second term). According to the wave equation this latter contribution can lead to the generation of radiation at the second-harmonic frequency. The first contribution in Eq. (5) does not lead to the generation of oscillating electromagnetic radiation (because its second time derivative vanishes); it leads to a process known as optical rectification, in which a static electric field is created across the nonlinear crystal. The second and third terms contains frequencies that are exactly twice the frequency of the fundamental wave.

Under certain conditions (like phase matching), it is possible to covert nearly all of the original frequency of the beam to the second harmonic frequency. Thus, second harmonic generation is a process where a wave at frequency *ω* is converted into one at frequency 2*ω,* such output is referred to as *second harmonic generation*. The second-order nonlinear effects can occur in the non-centrosymmetrical crystals only. In the dielectric dipole approximation, isotropic media and centrosymmetrical crystals cannot be used to generate second-order nonlinear effects. Therefore, the media for SHG should be the crystals having no inversion symmetry. This requirement is the same as that for the piezoelectric effect; thus all SHG crystals are piezoelectric crystals although the physical mechanisms for these two effects are not related to each other. One common use of second-harmonic generation is to convert the output of a fixed-frequency laser to a different spectral region. For example, the Nd:YAG laser operates in the near infrared at a wavelength of 1.06 µm. Second-harmonic generation is routinely used to convert the wavelength of the radiation to 0.53 um, in the middle of the visible spectrum.



**Figure 1. (a) Geometry of SHG. (b) Energy-level diagram of SHG**

Second-harmonic generation can be visualized by considering the interaction in terms of the exchange of photons between the various frequency components of the field. According to this picture, which is illustrated in part (b) of Fig.-1, two photons of frequency *ω* are destroyed, and a photon of frequency 2*ω* is simultaneously created in a single quantum-mechanical process. The solid line in the figure represents the atomic ground state, and the dashed lines represent what are known as virtual levels. These levels are not energy eigenlevels of the free atom but rather represent the combined energy of one of the energy eigenstates of of the atom and of one or more photons of the radiation field.

To date, SHG still is the most useful and well-developed technique for frequency up-conversion of laser beam or other coherent optical emission. In principle there are three basic designs for SHG devices, which are shown schematically in Fig.-2, featuring with (a) a single-pass configuration, (b) an external cavity configuration, and (c) an intracavity configuration. The design shown in Fig.-2, featuring with (a) it is most commonly employed geometry, it offers the advantage of simplicity and compactness; however, in this case, the conversion efficiency is usually limited to (30~50)%. In the case (b), the nonlinear crystal is placed in an external resonant cavity consisting of two mirrors. Mirror 1 has high reflectivity for the 2*ω* beam, while mirror 2 has a high reflectivity for the *ω* beam and a high transmissivity for the 2*ω* beam; so that one can except a higher intracavity intensity for the ω beam and a higher output coupling for the 2ω beam. Based on this design the highest conversion efficiency can be reached.



**Figure-2. Fundamental design for SHG devices**

The benefit of using an external cavity may be related to the increase of effective interaction length as well as the constructive interference enhancement of the intracavity intensity. In the case (c), the nonlinear crystal is placed inside the optical resonant cavity of the laser source itself. This design is mainly suitable for low-gain laser system in which the intracavity intensity of the lasing beam of ω is much higher than the output laser beam intensity. Placing the SHG crystal inside the laser cavity may lead to higher conversion efficiency. It is obvious that in the cases of (b) and (c) the advantage of simplicity and compactness no longer exists.Since the efficiency of SHG is determined by many factors, such as the fundamental-wave intensity, effective second-order susceptibility value, effective interaction length, as well as damage threshold for a given nonlinear crystal, there is no simple rule to determine which configuration is the best for a specific case; instead it is often a technical choice.

1. **Optical Sum- and Difference- Frequency Generation**

In the second-harmonic generation, considered the combination (addition) of two photons of the same frequency to produce a single photon of twice the frequency. It can now to generalize this process to allow for the case in which the two photons have different frequencies ω1 and ω2. In a similar fashion to our treatment of two photons with the same frequency, let us write the expression for the field as

or  (6)

which includes the complex conjugates of both *E*1 and *E*2. We again compute the second-order nonlinear polarizability assuming as in Eq.(1) that the second-order contribution to the nonlinear polarisation is of the form

 (7)

We have conveniently grouped common terms together. These include DC terms, second harmonic terms (involving 2*ω*1 and 2*ω*2), and two new terms involving *ω*1 + *ω*2 and *ω*1 - *ω*2. The new term involving *ω*1 + *ω*2 generates a new frequency that is the sum of the two original frequencies and is thus known as *sum frequency generation*. The term involving the difference between the two frequencies, *ω*1 - *ω*2 , is referred to as *difference frequency generation*. From the stand point of the photon picture, these two additional processes are shown in Fig. 3, with the virtual energy levels of the combined material-photon system. In the sum frequency generation, when a new photon *ω*3 =*ω*1 + *ω*2 is created, the frequencies *ω*1 and *ω*2 are destroyed Fig.-3(a). In the difference frequency generation, as shown in Fig.-3(b), the photon of higher frequency *ω*1 is destroyed while both *ω*2 and *ω*3 are created. Since *ω*2is already present as one of the input beams, this suggests that *ω*2 is amplified in the process-that is, photons are added to the beam at the frequency*ω*2.

The processes of sum and difference frequency generation can very useful, not only in generating specific frequencies at new wavelengths but also in generating new tunable frequencies at new wavelengths. For example, an intense single-frequency laser can serve as the *ω*1 in these processes and a lower-power tunable laser can provide the *ω*2 and so obtain strong signals at either *ω*1 + *ω*2 or *ω*1 - *ω*2. All of the frequencies 2*ω*1, 2*ω*2, *ω*1 + *ω*2 and *ω*1 - *ω*2 might simultaneously be generated when two input beams of frequency *ω*1 and *ω*2 are transmitted through the optical material.

There is a constraint known as *phase matching* that must be implemented in order to efficiently generate any of those additional frequencies, yet phase matching can be applied to only one of those processes at a time, it is applicable to all of the nonlinear processes.



**Figure-3. (a) sum frequency generation; (b) difference frequency generation**

The phase matching can be achieved and the sum-frequency wave can be effectively generated only in the condition of

  (8)

In general, owing to dispersion effect we always have *k*3≠ (*k*1 + *k*2), i.e., the phase-velocity of the polarization wave of ***P***(2)(*ω*3) is different from that of the radiation wave of ***E***(*ω*3); therefore, the power transfer among the three optical waves cannot take place effectively. Here k1and k2, and k3 are wave vectors of these three waves. However, as we can use the birefringence effect of the refractive index to compensate the dispersion effect in a second-order nonlinear crystal.

Similiarly in difference-frequency generation if , the power transfer among the three optical waves cannot take place effectively. Only in the case of

  (9)

**3. Optical Parametric Oscillation**

The amplification can be enhanced by placing the optical harmonic (nonlinear) crystal within an optical cavity in which the mirrors are specifically made reflective at either one of these two frequencies, or for both. Thus the intensity at those frequencies will build up within the cavity, by Fabry-Perot interferometer. Such an amplification process is known as an optical parametric oscillator (OPO). In the process of difference frequency mixing, the frequency *ω*2 is amplified while the frequency *ω*3 is being generated. In the process of optical parametric oscillation (OPO) the intense input laser beam at frequency *ω*p is known as the *pump* frequency, when passes through a nonlinear material, generates the desired frequencies *ω*s (signal frequency) and the frequency *ω*i (idler frequency) shown in Fig-4.



**Figure-4. Optical parametric oscillation**

Of course, either *ω*s or *ω*i can be tunable laser to generate amplified tunable output. This process is used most often in the infrared frequency range, where tunable lasers are not as readily available as in the visible portion of the frequency spectrum. The output of an optical parametric oscillator (OPO) is similar to that of a laser. It is highly monochromatic and exhibits laser speckle. The energy conservation requires that

  (10)

Here *ω*p, *ω*s, and *ω*i are the frequencies of the pump, signal and idler wave. It is clear that the frequencies of the two emitted photons cannot be uniquely determined on the basis of the energy conservation condition, (10) alone. For a given *ω*p, there can be a continuous range of choices of *ω*s and *ω*i. This, in fact, is the origin of the tunability of the optical parametric oscillator. The specific pair of frequencies that will be emitted is dictated by the momentum conservation condition, or phase matching condition: ***k***p = ***k***s + ***k***i, that must also be satisfied in order to ensure that the signal waves generated in different parts of the nonlinear crystal are in phase and add coherently. For collinearly propagating waves this may be written

  (11)

Here *n*p, *n*s and *n*i are the refractive indices of the pump, signal and idler wave and *λ*p, *λ*s and *λ*i there corresponding wavelengths respectively. The pump signal is usually provided by a laser and, therefore *λ*p is fixed. However, if the refractive indices are varied, the signal and idler frequencies will tune. Under an appropriate arrangement for the angle (or temperature) of a given nonlinear crystal, the above two requirements (Eq. (10) & (11) can be satisfied and oscillations at two different frequencies *ω*s, and *ω*i can be achieved. Based on this working condition, if we slightly change the angle or temperature of the crystal, the refractive index relation between these three waves will be changed; therefore the oscillating frequencies will be smoothly tuned to different values. For some nonlinear crystals, which possess a larger electro-optical or magneto-optical effect or refractive index, the oscillating frequency can also be tuned by applying an external electric or magnetic dc field.

The requirements of nonlinear crystals for optical parametric oscillation are essentially the same as that for SHG. In other words, the nonlinear materials must be non-centrosymmetrical crystals, highly transparent for pump, signal, and idler beams, able to fulfill the phase matching by using angle-tuning or temperature-tuning. In principle, all commonly used SHG crystals listed in Table-1, can be employed for optical parametric oscillation purposes. A possible simple implementation of the optical parametric oscillator is shown schematically in Figure-5. It is consist of a suitably oriented nonlinear optical crystal in a Fabry-Perot cavity. The cavity mirrors are coated to transmit the pump wave and reflect either the signal wave only or both the signal and idler waves. In the former case, the oscillator is known as the singly resonant oscillator, and, in the latter case, it is known as the doubly resonant oscillator. After passing through the output-coupling mirror the transmitted pump beam is blocked by a filter. The further separation between the signal beam and idler beam can be done by using appropriate spectral filters or optical dispersive elements. Various optical cavity designs, including stable, unstable, or metastable cavity configurations, can be employed for OPO purpose. The criteria of selection of cavity designs are same as that for laser cavity devices.



**Figure-5. Singly-Resonant Optical Parametric Oscillator**

Where Δ*k* = *k*p – *k*s – *k*i is the phase mismatch factor. The fundamental coupled equations for parametric oscillation are similar to those of second harmonic generations.

**Nonlinear Optical (NLO) Materials**

For generating new frequencies from existing lasers via harmonic generation, there has been an extensive effort in recent years to identify effective materials for such processes. In addition to having a large nonlinearity, these materials must be transparent not only at the laser frequency but also at the newly generated frequency. These materials must (1) be resistant to optical damage, (2) have high mechanical hardness, (3) exhibit good thermal and chemical stability, (4) be capable of being grown in useful sizes, and (5) have the appropriate phase-matching properties. The second harmonic crystals must have no inversion symmetry (i.e. non-centrosymmetric). Bulk second-order nonlinear materials are generally inorganic crystals. A number of semiconductors are useful for second harmonic generation when used in waveguides.The nonlinear crystals can be classified into two groups according to their physical properties. Crystals grown from water solutions are fragile, hygroscopic, and sensitive to thermal shock. The crystals of this group, to which KDP and its isomorphs belong, are somewhat difficult to handle because the crystals are soft, and the polished faces may be fogged if they are held with bare hands or exposed to humid atmosphere. On the other hand, the crystals are easy to grow, they are available in large sizes, and they are of excellent optical quality. Crystals grown from the melt are relatively hard, nonhygroscopic and less sensitive to thermal shock. Important members of this group crystals are LiNbO3 and Ba2NaNb5O15. The optical quality is usually inferior to water grown crystals because of refractive index nonuniformities associated with the crystal growth condition. Table-1, lists the primary nonlinear materials which are used in conjunction with solid state-lasers.

Inorganic crystals such as barium borate (BBO), zinc oxide (ZnO), and potassium dihydrogen phosphate (KDP) are well-established and widely used for frequency upconversion in laser systems, as they combine large second-order NLO susceptibilities with high damage thresholds. Organic NLO materials, on the other hand, have been demonstrated to feature various advantages, including very high molecular hyperpolarizabilities, a large diversity of structures and ease of processing.

The fact that molecular structures of organic NLO dyes can be designed and synthesized with a large flexibility, together with the exploitation of multiple synergetic supramolecular interactions allows the construction of hierarchical self-assembled architectures on the micro- and nanoscale. This results in subwavelength scale materials with well-defined structures and highly anisotropic optical properties that could serve as building blocks for integrated photonic circuits. However, the polar nature of many of these organic molecules leads to a strong tendency to create self-organized centrosymmetric structures driven by dipole-dipole interactions, hampering their applications in second-order NLO. In addition, organic molecules can generally sustain much lower laser intensities before photo-chemical reactions set in, leading to lower damage thresholds. Therefore, despite a lot of research activities in the end of the last century, the development of organic molecular materials for practical applications in the field of nonlinear optics has been limited.

**Some important Nonlinear Optical Crystals**

1. **Potassium dihydrogen phosphate (KDP) family:** Monopotassium phosphate (MKP) (also, potassium dihydrogenphosphate, KDP, or monobasic potassium phosphate) is the [inorganic compound](https://en.wikipedia.org/wiki/Inorganic_compound) with the formula KH2PO4. Together with [dipotassium phosphate](https://en.wikipedia.org/wiki/Dipotassium_phosphate%22%20%5Co%20%22Dipotassium%20phosphate) (K2HPO4.(H2O)x) it is often used as a [fertilizer](https://en.wikipedia.org/wiki/Fertilizer), [food additive](https://en.wikipedia.org/wiki/Food_additive), and [buffering agent](https://en.wikipedia.org/wiki/Buffering_agent). The salt often cocrystallizes with the dipotassium salt as well as with [phosphoric acid](https://en.wikipedia.org/wiki/Phosphoric_acid). [Single crystals](https://en.wikipedia.org/wiki/Single_crystal) are [paraelectric](https://en.wikipedia.org/wiki/Paraelectric%22%20%5Co%20%22Paraelectric) at room temperature. At temperatures below −150 °C (−238 °F), they become [ferroelectric](https://en.wikipedia.org/wiki/Ferroelectric). Deuterated potassium dihydrogen phosphate (KD2PO4) or DKDP [single crystals](https://en.wikipedia.org/wiki/Single_crystal) are widely used in [non-linear optics](https://en.wikipedia.org/wiki/Non-linear_optics) as the second, third and fourth harmonic generators for [Nd:YAG](https://en.wikipedia.org/wiki/Nd%3AYAG%22%20%5Co%20%22Nd%3AYAG) and [Nd:YLF](https://en.wikipedia.org/wiki/Nd%3AYLF%22%20%5Co%20%22Nd%3AYLF) lasers. They are also found in [electro-optical](https://en.wikipedia.org/wiki/Electro-optical) application as [Q-switches](https://en.wikipedia.org/wiki/Q-switching) for [Nd:YAG](https://en.wikipedia.org/wiki/Nd%3AYAG%22%20%5Co%20%22Nd%3AYAG), [Nd:YLF](https://en.wikipedia.org/wiki/Nd%3AYLF%22%20%5Co%20%22Nd%3AYLF), [Alexandrite](https://en.wikipedia.org/wiki/Alexandrite) and [Ti-sapphire lasers](https://en.wikipedia.org/wiki/Ti-sapphire_laser), as well as for [Pockels cells](https://en.wikipedia.org/wiki/Pockels_effect%22%20%5Co%20%22Pockels%20effect). DKDP is closely related to [monopotassium phosphate](https://en.wikipedia.org/wiki/Monopotassium_phosphate%22%20%5Co%20%22Monopotassium%20phosphate) or KDP or KH2PO4. Replacement of hydrogen by [deuterium](https://en.wikipedia.org/wiki/Deuterium) in DKDP lowers the frequency of O-H vibrations and their [overtones](https://en.wikipedia.org/wiki/Overtones) (high-order harmonics). Absorption of light by those overtones is detrimental for the infrared lasers, which DKDP and KDP crystals are used for. Consequently, despite higher cost, DKDP is more popular than KDP. DKDP crystals are grown by a water-solution method at usual level of deuteration >98%.

Potassium dihydrogenphosphate, KDP can exist in several [polymorphs](https://en.wikipedia.org/wiki/Polymorphism_%28materials_science%29). At room temperature it forms [paraelectric](https://en.wikipedia.org/wiki/Paraelectric%22%20%5Co%20%22Paraelectric) crystals with tetragonal symmetry. Upon cooling to −150 °C (−238 °F) it transforms to a [ferroelectric](https://en.wikipedia.org/wiki/Ferroelectric) phase of orthorhombic symmetry, and the transition temperature shifts up to −50 °C (−58 °F) when hydrogen is replaced by deuterium. Heating to 190 °C (374 °F) changes its structure to monoclinic. When heated further, MKP decomposes, by loss of water, to potassium metaphosphate, KPO3, at 400 °C (752 °F).

The crystals of this family have proven to be the most important group of useful second-harmonic generators. The crystals which are all negative uniaxial includes KDP, ADP, and CDA, belong to point group and, thus, have a tetragonal symmetry. The crystals are grown at room temperature from a water solution and therefore are exceptionally hygroscopic. Due to the hygroscopic nature of the crystals, they are often polished in solutions of ethylene glycol rather than in water. However, the ease of crystal growth means that it is possible to obtain large crystals of very high optical quality. Most members of the KDP family have a high damage threshold for optically induced damage. Transparency exists from 0.22 to 1.6 μm for the phosphates, and from about 0.26 to 1.6 μm for arsenates. Deuterated forms of the crystals are also available and are indicated by the notation D\*. Deuteration increases the infrared limit to about 1.9 μm. KDP possesses an absorption band at 1 to 1.2 μm, so KD\*P is preferred over KDP for Nd:YAG and Nd:glass lasers. The greatest attributes of this family of crystals as a nonlinear device material are their resistance to laser damage and their high optical quality. Opposing these advantages, there are several disadvantages. The materials have fairly low refractive indices, typically 1.50 to 1.55, so that they also have small nonlinear coefficients. All of the KDP isomorphs are water-soluble and have a maximum safe operating temperature of about 100 0C. The crystals are fragile and sensitive to thermal shock as well as hairline fractures, and should be heated slowly at a rate of less than about 5 0C/min.Isomorphs of these materials have similarly been used in nonlinear optics, the most widely known isomorphs being deuterated KDP, which is normally designated as KD\*P. Some of the other isomorphs have been used because the temperature dependence of their refractive index allows 900phase matching for particular interactions. CDA and CD\*A 900 phase-match the important 1.06-μm transition of Nd:YAG and Nd:glass, RDP and RDA are mainly employed to frequency-doubled the output from the ruby lasers.

**2. Lithium niobate (LiNBO3**): Lithium niobate ([Li](https://en.wikipedia.org/wiki/Lithium)[Nb](https://en.wikipedia.org/wiki/Niobium)[O](https://en.wikipedia.org/wiki/Oxygen)3) is a synthetic [salt](https://en.wikipedia.org/wiki/Salt_%28chemistry%29) consisting of [niobium](https://en.wikipedia.org/wiki/Niobium), [lithium](https://en.wikipedia.org/wiki/Lithium), and [oxygen](https://en.wikipedia.org/wiki/Oxygen). Its single crystals are an important material for optical waveguides, mobile phones, piezoelectric sensors, optical modulators and various other linear and non-linear optical applications. Lithium niobate is sometimes referred to by the brand name linobate. Lithium niobate is a colorless solid, and it is insoluble in water. It has a [trigonal](https://en.wikipedia.org/wiki/Trigonal%22%20%5Co%20%22Trigonal) [crystal system](https://en.wikipedia.org/wiki/Crystal_system), which lacks [inversion symmetry](https://en.wikipedia.org/wiki/Inversion_symmetry) and displays [ferroelectricity](https://en.wikipedia.org/wiki/Ferroelectricity%22%20%5Co%20%22Ferroelectricity), the Pockel Effect, the [piezoelectric](https://en.wikipedia.org/wiki/Piezoelectric) effect, [photoelasticity](https://en.wikipedia.org/wiki/Photoelasticity%22%20%5Co%20%22Photoelasticity) and nonlinear optical polarizability. Lithium niobate has negative uniaxial [birefringence](https://en.wikipedia.org/wiki/Birefringence) which depends slightly on the [stoichiometry](https://en.wikipedia.org/wiki/Stoichiometry%22%20%5Co%20%22Stoichiometry) of the crystal and on temperature. It is transparent for wavelengths between 350 and 5200 [nanometers](https://en.wikipedia.org/wiki/Nanometer). Lithium niobate can be [doped](https://en.wikipedia.org/wiki/Dopant) by [magnesium oxide](https://en.wikipedia.org/wiki/Magnesium_oxide), which increases its resistance to optical damage (also known as photorefractive damage) when doped above the [optical damage threshold](https://en.wikipedia.org/w/index.php?title=Optical_damage_threshold&action=edit&redlink=1). Other available dopants are [iron](https://en.wikipedia.org/wiki/Iron), [zinc](https://en.wikipedia.org/wiki/Zinc), [hafnium](https://en.wikipedia.org/wiki/Hafnium), [copper](https://en.wikipedia.org/wiki/Copper), [gadolinium](https://en.wikipedia.org/wiki/Gadolinium), [erbium](https://en.wikipedia.org/wiki/Erbium), [yttrium](https://en.wikipedia.org/wiki/Yttrium),  [manganese](https://en.wikipedia.org/wiki/Manganese)  and [boron](https://en.wikipedia.org/wiki/Boron).

LiNBO3 is a 3m negative uniaxial crystal with trigonal symmetry. LiNBO3 crystals are grown from the melt by a Czochralski process. This material is nonhygroscopic and hard, taking a good polish readily. In addition, they have a much higher nonlinear coefficient than members of the KDP family. However, LiNBO3 has a significantly lower damage threshold than members of the KDP family. In addition, many crystals of LiNBO3 are susceptible to a type of damage (often referred to a photorefractive damage) that alters the index of refraction within the crystal. The crystals of lithium niobate are transparent in the region 0.42 to 5.2 μm. Temperature sensitivity of birefringence is such that, by varying temperature, phase matching can be achieved to 900 to the optical axis. Doping LiNBO3 with MgO reduces the photorefractive damage and permits 90-degree phase matching at a temperature of 107 0C. LiNBO3 is most commonly used as a doubling crystal for internally frequency-doubled Nd:YAG lasers, and for lower-power externally frequency-doubled Nd:YAG and Nd:glass lasers.

**3. Potassium titalyl phosphate (KTP):** Potassium titanyl phosphate (KTP) is an [inorganic compound](https://en.wikipedia.org/wiki/Inorganic_compound) with the formula KTiOPO4. It is a white solid. KTP is an important [nonlinear optical](https://en.wikipedia.org/wiki/Nonlinear_optics) material that is commonly used for [frequency-doubling](https://en.wikipedia.org/wiki/Second-harmonic_generation) [diode-pumped solid-state lasers](https://en.wikipedia.org/wiki/Diode-pumped_solid-state_laser) such as [Nd:YAG](https://en.wikipedia.org/wiki/Nd%3AYAG_laser%22%20%5Co%20%22Nd%3AYAG%20laser) and other [neodymium](https://en.wikipedia.org/wiki/Neodymium)-doped [lasers](https://en.wikipedia.org/wiki/Laser). The compound is prepared by the reaction of [titanium dioxide](https://en.wikipedia.org/wiki/Titanium_dioxide) with a mixture of KH2PO4 and K2HPO4 near 1300 K. The potassium salts serve both as reagents and flux. The material has been characterized by [X-ray crystallography](https://en.wikipedia.org/wiki/X-ray_crystallography). KTP has an [orthorhombic](https://en.wikipedia.org/wiki/Orthorhombic) [crystal structure](https://en.wikipedia.org/wiki/Crystal_structure). It features octahedral Ti(IV) and tetrahedral phosphate sites. Potassium has a high coordination number. All heavy atoms (Ti, P, K) are linked exclusively by oxides, which interconnect these atoms. Crystals of KTP are highly transparent for wavelengths between 350–2700 nm with a reduced transmission out to 4500 nm where the crystal is effectively opaque. Its [second-harmonic generation](https://en.wikipedia.org/wiki/Second-harmonic_generation) (SHG) coefficient is about three times higher than [KDP](https://en.wikipedia.org/wiki/Potassium_dihydrogen_phosphate). It has a [Mohs hardness](https://en.wikipedia.org/wiki/Mohs_scale_of_mineral_hardness%22%20%5Co%20%22Mohs%20scale%20of%20mineral%20hardness) of about 5. KTP is also used as an [optical parametric oscillator](https://en.wikipedia.org/wiki/Optical_parametric_oscillator) for [near IR](https://en.wikipedia.org/wiki/Infrared) generation up to 4 µm. It is particularly suited to high power operation as an optical parametric oscillator due to its high [damage threshold](https://en.wikipedia.org/wiki/Laser_damage_threshold) and large crystal aperture. The high degree of [birefringent](https://en.wikipedia.org/wiki/Birefringence%22%20%5Co%20%22Birefringence) walk-off between the pump signal and idler beams present in this material limit its use as an optical parametric oscillator for very low power applications.

The material has a relatively high threshold to optical damage (~15 J/cm²), an excellent optical nonlinearity and excellent thermal stability in theory. In practice, KTP crystals need to have stable temperature to operate if they are pumped with 1064 nm ([infrared](https://en.wikipedia.org/wiki/Infrared), to output 532 nm green). However, it is prone to [photochromic](https://en.wikipedia.org/wiki/Photochromic%22%20%5Co%20%22Photochromic) damage (called grey tracking) during high-power 1064 nm second-harmonic generation which tends to limit its use to low- and mid-power systems.

KTP (KTiOPO4) is a mm2 biaxial crystal with orthorhombic symmetry. KTP is a difficult crystal to grow, and is currently grown by hydrothermal and flux growth techniques. However, KTP possesses good optical properties, a large acceptance angle, large temperature acceptance, a large nonlinear coefficient, and high optical damage thresholds. It is a mechanically rugged and nonhygroscopic crystal. However KTP suffers from a cumulative photochemical degradation phenomena, termed *grey tracking*, caused by long-term exposure to the intense fundamental and second harmonic radiation. Although this photochemical effect can be reversed by operating the crystal at an elevated temperature, absorption in the crystal due to the grey tracking may damage the crystal beyond repair. KTP is a more recently developed crystal than KDP or LiNbO3, but is emerging as one of the most popular frequency-doubling crystals for Nd:YAG and Nd:glass lasers. KTP is also finding application as an OPO material and in difference frequency application.

**4. Beta-barium borate (BBO):** Barium borate is an [inorganic compound](https://en.wikipedia.org/wiki/Inorganic_compound), a [borate](https://en.wikipedia.org/wiki/Borate) of [barium](https://en.wikipedia.org/wiki/Barium) with a chemical formula BaB2O4 or Ba(BO2)2. It is available as a [hydrate](https://en.wikipedia.org/wiki/Hydrate) or dehydrated form, as white powder or colorless crystals. The crystals exist in the high-temperature α phase and low-temperature β phase, abbreviated as BBO; both phases are [birefringent](https://en.wikipedia.org/wiki/Birefringent%22%20%5Co%20%22Birefringent), and BBO is a common [nonlinear optical](https://en.wikipedia.org/wiki/Nonlinear_optical) material. Barium borate exists in three major crystalline forms: alpha, beta, and gamma. The low-temperature beta phase converts into the alpha phase upon heating to 925 °C. β-Barium borate (BBO) differs from the α form by the positions of the barium ions within the crystal. Both phases are birefringent, however the α phase possesses centric symmetry and thus does not have the same nonlinear properties as the β phase.

Alpha barium borate, α-BaB2O4 is an optical material with a very wide optical transmission window from about 190 nm to 3500 nm. It has good mechanical properties and is a suitable material for high-power [ultraviolet](https://en.wikipedia.org/wiki/Ultraviolet) [polarization](https://en.wikipedia.org/wiki/Polarization_%28waves%29) [optics](https://en.wikipedia.org/wiki/Optics).[[5]](https://en.wikipedia.org/wiki/Barium_borate#cite_note-5) It can replace [calcite](https://en.wikipedia.org/wiki/Calcite), [titanium dioxide](https://en.wikipedia.org/wiki/Titanium_dioxide) or [lithium niobate](https://en.wikipedia.org/wiki/Lithium_niobate) in [Glan–Taylor prisms](https://en.wikipedia.org/wiki/Glan%E2%80%93Taylor_prism%22%20%5Co%20%22Glan%E2%80%93Taylor%20prism), [Glan–Thompson prisms](https://en.wikipedia.org/wiki/Glan%E2%80%93Thompson_prism%22%20%5Co%20%22Glan%E2%80%93Thompson%20prism), walk-off [beam splitters](https://en.wikipedia.org/wiki/Beam_splitter) and other optical components. It has low [hygroscopicity](https://en.wikipedia.org/wiki/Hygroscopic%22%20%5Co%20%22Hygroscopic), and its [Mohs hardness](https://en.wikipedia.org/wiki/Mohs_hardness%22%20%5Co%20%22Mohs%20hardness) is 4.5. Its [damage threshold](https://en.wikipedia.org/wiki/Laser_damage_threshold) is 1 GW/cm2 at 1064 nm and 500 MW/cm2 at 355 nm.Beta barium borate, β-BaB2O4, is a [nonlinear optical material](https://en.wikipedia.org/wiki/Nonlinear_optics) transparent in the range ~190–3300 nm. It can be used for [spontaneous parametric down-conversion](https://en.wikipedia.org/wiki/Spontaneous_parametric_down-conversion). Its [Mohs hardness](https://en.wikipedia.org/wiki/Mohs_hardness%22%20%5Co%20%22Mohs%20hardness) is also 4.5. Gamma barium borate, γ-BaB2O4, discovered recently, was produced by heating beta barium borate 900 °C under 3 GPa of pressure. It was found to have a monoclinic crystal structure.

Barium borate has strong negative uniaxial [birefringence](https://en.wikipedia.org/wiki/Birefringence) and can be phase-matched for type I (*ooe*) [second-harmonic generation](https://en.wikipedia.org/wiki/Second-harmonic_generation) from 409.6 to 3500 nm. The temperature sensitivity of the indices of refraction is low, leading to an unusually large (55 °C) temperature phase-matching bandwidth.

BBO (β-BaB2O4) is a 3m negative uniaxial crystal with trigonal symmetry. The crystal possesses a moderate nonlinear coefficient, high-temperature stability, and an outstanding damage threshold. It is mildly hygroscopic, typically requiring a special housing under laboratory conditions. The crystal’s optical transmission also extends down to 200nm, making it possible to perform multiphoton nonlinear processes into the blue and UV. However, BBO also possesses a very low angular tolerance, meaning that good alignment and high-quality optical beams are required for efficient nonlinear conversion. The large walk-off angle also results in beams that are elliptical. Due to its broad phase-matching region. BBO finds good application for harmonic generations. It also is finding application in broadly tunable OPOs and optical parametric amplifiers (OPAs). The exceptionally high IR transmittance allows high average power OPO and OPA operation with minimal thermal heating caused by the idler radiation.

**5. Barium sodium niobate (Ba2NaNb5O15):** Barium sodium niobate (Ba2NaNb5O15) has been shown to be an outstanding material for electrooptic and nonlinear optic applications, and is particularly useful for the second harmonic generation of 0.53 radiation from 1.06 microns and for the parametric conversion of 0.53 micron radiation to longer wavelengths. The material was discovered in 1967 by researchers at the Bell Telephone Laboratories and was found to be stable to intense visible radiation (laser beams) and to have a number of useful nonlinear, electro-optic and piezoelectric properties. Barium sodium niobate is phase matchable without double refraction; its nonlinear coefficients are approximately twice those observed in lithium niobate, and it is stable under intense laser radiation. A most important practical feature is the fact that the phase-match temperatures are quite reproducible from crystal to crystal, the variations being less than 10°C.

Ba2NaNb5O15 is a mm2 biaxial crystal with orthorhombic symmetry. However, since *n*x≈*n*y to a first approximation, at least insofar as the gross properties of phase matching are concerned, the crystal can be assumed to be uniaxial. It is mechanically hard, nonhygroscopic crystal with good chemical stability and UV transparency. It possesses a moderate nonlinear coefficient and good optical damage thresholds. This freedom from damage, combined with 900 phase matching, has made possible very efficient second-harmonic generation from a continuous-wave Nd:YAG laser, providing an intense source of 5300 Å radiation. However, the use of Ba2NaNb5O15, which transmits light in the region 0.46 to 1.1 μm, presents other problems. Great difficulties are involved in preparing high optical quality crystals and are no longer available commercially. Commercially available crystals suffer from situation, scatter centers, and built-in strain. The most persistent defect are growth striations which are periodic variations of refractive index normal to the growth direction. Light is diffracted and refracted by these index variations, making good phase matching very difficult to achieve. Ba2NaNb5O15 or “Banana” crystals were a popular nonlinear material in the mid-1970s.

**6. Lithium iodate (LiIO3) and Lithium formate monohydrate:** Lithium iodate (LiIO3) is a negative uniaxial crystal for nonlinear, acousto-optical and piezoelectric applications. It has been utilized for 347 nm ruby lasers. [Mohs hardness](https://en.wikipedia.org/wiki/Mohs_hardness) of lithium iodate is 3.5–4. Its linear [thermal expansion](https://en.wikipedia.org/wiki/Thermal_expansion) coefficient at 298 K (25 °C; 77 °F) is 2.8·10−5/°C (a-axis) and 4.8·10−5/°C (c-axis). Its transition to β-form begin at 50 °C (122 °F) and it is irreversible.

LiIO3 is a 6 crystal with hexagonal symmetry. The crystal is hygroscopic and significantly more fragile than LiNbO3. In addition, this crystal has a rather low optical-damage threshold. However, the crystal does have a high nonlinear coefficient and does not suffer from the photorefractive damage of LiNbO3. LiIO3 crystals are transparent in the region 0.32 to 5.0 μm, while formate crystals are transparent in the 0.25 to 1.2μm range. Both crystals are grown from water solutions. Lithium iodate has nonlinear coefficients which are comparable to those of lithium niobate, although it does not suffer from the refractive index damage problems that plague the niobate. Also LiIO3 possesses an optical quality which is far superior to Ba2NaNb5O15. Consequently, lithium iodate has found application in efficient intracavity second-harmonic generation in Nd:YAG lasers. Since the refractive indices are very stable with respect to temperature, phase matching is achieved by angle tuning. Interesting features of the formate crystals are a near noncritical phase matching for Nd laser radiation and an insensitivity of the phase-match direction to temperature changes.

**7. Lithium tri-borate (LBO):** Lithium triborate (LiB3O5) or LBO is a [non-linear optical](https://en.wikipedia.org/wiki/Non-linear_optics) [crystal](https://en.wikipedia.org/wiki/Crystal). It has a wide [transparency](https://en.wikipedia.org/wiki/Transparency_%28optics%29) range, moderately high nonlinear coupling, high damage threshold and desirable [chemical](https://en.wikipedia.org/wiki/Chemical) and [mechanical](https://en.wikipedia.org/wiki/Mechanics) properties. This crystal is often used for [second harmonic generation](https://en.wikipedia.org/wiki/Second_harmonic_generation) (SHG, also known as *frequency doubling*), for example of [Nd:YAG lasers](https://en.wikipedia.org/wiki/Nd%3AYAG_laser%22%20%5Co%20%22Nd%3AYAG%20laser) (1064 nm → 532 nm). LBO can be both critically and non-critically [phase-matched](https://en.wikipedia.org/wiki/Phase_matching). In the latter case the crystal has to be heated or cooled depending on the [wavelength](https://en.wikipedia.org/wiki/Wavelength). Lithium triborate (LBO) crystals are applicable in various nonlinear optical applications, such as [Frequency doubling (SHG)](https://en.wikipedia.org/wiki/Second-harmonic_generation) and frequency tripling of high peak power pulsed Nd doped, [Ti:Sapphire lasers](https://en.wikipedia.org/wiki/Ti-sapphire_laser%22%20%5Co%20%22Ti-sapphire%20laser) and [Dye lasers](https://en.wikipedia.org/wiki/Dye_laser), NCPM (non-critical phase matching for frequency conversion of CW and quasi CW radiation, OPO ([Optical parametric oscillator](https://en.wikipedia.org/wiki/Optical_parametric_oscillator)) of both Type 1 and Type 2 phase-matching.

LBO is a mm2 biaxial crystal with orthorhombic symmetry. It is a mechanically hard, nonhygroscopic crystal with good chemical stability and UV transparency. It possesses a moderate nonlinear coefficient and good optical damage thresholds. This crystal has a transparency range extends down to 160 nm and absorption is from 170 nm to 2.6 μm. It offers smallest walk- off angle and widest acceptance angle for both type-I and type-II phase matching for SHG and THG of Nd:YAG laser.

**Other Materials for Second Harmonic Generations**

So far we have only considered inorganic piezoelectric crystals as the major second-order nonlinear materials for highly efficient SHG, OPO and OPA. Actually researchers have also paid considerable attention to exploiting organic bulk crystals for SHG. Of all the reported organic materials for second-order nonlinear optical applications, the crystals of urea, NPP [N-(4-nitrophenyl)-L-prolinol], and DAST [4-dimethylamino-N-Methystilbazolium tosylate] can offer a superior performance for SHG of OPO. Compared to inorganic crystals, the organic compounds may have higher second-order nonlinearity, but sometimes might be limited by the available crystal size and lower optical damage threshold.

**Table-1 Nonlinear Optical Crystals**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Crystal** | **Crystal Class** | **Transparent range****(μm)** | ***dil*****(10-12 m/V)** | **Phase matching** | **Damage Threshold****(MW / cm2)** | **Efficiency (%)** |
| KH2PO4(KDP) |  (a) | 0.2 – 1.5 | *d36* = 0.39 | ϕ -Tuning | ~ 500 | 20 -30 |
| KD2PO4(KD\*P) |  (a) | 0.2 – 1.5 | *d36* = 0.37 | ϕ -Tuning | ~ 1000 | 20 -40 |
| NH4H2PO4(ADP) |  (a) | 0.2 – 1.2 | *d36* = 0.47 | ϕ -Tuning | ~ 500 | 20 -30 |
| KNbO3(KN) | *mm*2 (b) | 0.4 - 5 | *d31* = 12.8 | T-Tuning | > 500 | 30 ~ 60 |
| β-BaB2O4(BBO) | 3*m* (a) | 0.19 - 3 | *d22* = 2.3 | ϕ -Tuning | ~1500 | 40 ~ 60 |
| LiB3O5(LBO) | *mm*2 (b) | 0.16 – 2.6 | *d31* = 0.85 | ϕ -Tuning | ~ 2000 | 40 ~ 60 |
| KTiOPO4(KTP) | *mm*2 (b) | 0.3 – 5.3 | *d24* = 3.3 | ϕ -Tuning | ~ 500 | 40 ~ 60 |
| LiNbO3(LN) | 3*m* (a) | 0.33 - 5 | *d31* = -5.3*d22* = 2.1 | T-Tuning | ~ 100 | 30 ~ 50 |
| LiIO3 | 6 (a) | 0.3 – 5.5 | *d31* = 5.4 | ϕ -Tuning | ~ 100 | 30 ~ 50 |
| CsH2AsO4(CDA) |  (a) | 0.26 – 1.43 | *d*36 = 0.40 | ϕ -TuningT-Tuning | ~ 500 | 30 ~ 50 |
| RbH2AsO4(RDA) |  (a) | 0.26 – 1.46 | *d*36 = 0.39(0.694 μm) | ϕ -TuningT-Tuning | ~ 350(0.694 μm) | 30 ~ 50 |
| RbH2PO4(RDP) |  (a) | 0.22 – 1.4 | *d*36 = 0.4 | ϕ -Tuning | ~ 300 | 30 ~ 50 |
| AgGaSe2 |  (a) | 0.7 – 18 | *d*36 = 33(10.6 μm) | ϕ -Tuning | ~ 350(10.6 μm) | 5 ~ 10 |
| Ag3AsS3 | 3*m* (a) | 0.6 – 13 | *d*15 = 11*d*22 = 18(10.6 μm) | ϕ -Tuning | ~ 30(10.6 μm) | 5 ~ 10 |
| CdGeAs2 |  (a) | 2.4 – 18 | *d*36 = 235(10.6 μm) | ϕ -Tuning | ~ 40(10.6 μm) | 10 ~ 20 |

(a) Negative uniaxial crystal, (b) Negative biaxial crystal, and (c) Positive uniaxial crystal.

**ϕ -Tuning**: angle tuning; **T –Tuning**: temperature tuning.

**Material Parameters:**

For the design of a device such as a frequency doubler or parametric oscillator, physical properties of the nonlinear material, such the value of the nonlinear coefficient, damage threshold, absorption losses, and phase-matching parameters, are of importance. For the updated OPO devices pumped with high-peak power pulsed laser beam, the conversion efficiency from the pump pulse energy to the output pulse energy can be higher than (50 ~ 70) %. The interest in OPOs, demonstrated as far back as 1965, has been revived recently due to the availability of efficient nonlinear crystals, LD pumped laser systems and high damage threshold optics. Beta Barium Borate (BBO), Lithium Triborate (LBO), Cesium Lithium borate (CLBO) and Potassium Titanyl Phosphate (KTP) have superior properties listed in Table-1 for application in the uv-near IR optical band. These include a high effective nonlinear coefficient, good optical transparency, small walk-off and a high laser damage threshold.

KTP has a relatively large effective nonlinear coefficient and transmission in the near-infrared with moderate walk-off and damage threshold which makes it an excellent crystal for near-infrared applications. Its high resistance to moisture is most advantageous for use in the laboratory environment. KTP gives very good efficiency for OPO of Nd:YAG laser due to quasi-critical phase matching (θ = 900; φ~ 240) scheme which has low walk-off, high angular acceptance and high effective nonlinear coefficient. Walk-off in acentric birefringent crystals like KTP results poor coupling between the interacting ordinary and extraordinary waves and therefore in low conversion efficiencies. Walk-off becomes zero when the pump beam propagates in a principal plane of the crystal. The values of the angular and spectral acceptance bandwidth of the crystal are decided by the particular phase matching scheme and impose a limit on the pump divergence and spectral width. The nonlinear coefficients of KDP and its isomorphs are all within a factor of 2. ADP has the largest and RDA has the smallest nonlinear coefficient.

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