Kirk-Othmer Encyclopedia of Chemical Technology.

CERAMICS, NONLINEAR OPTICAL AND ELECTROOPTIC CERAMICS

1. Nonlinear Optical Effects

When an intense beam of light from a laser (see Lasers) passes through certain transparent crystals, a portion of the beam emerges having a wavelength equal to half that of the incident beam. This effect, known as frequency doubling or second harmonic generation, takes place in a large number of crystalline materials at a wide range of wavelengths. The wavelength of the frequency-doubled beam depends on the incident wavelength and not the crystal used. The effect results from changes in the polarizability of the electrons in the crystal under the influence of intense light. In fact, in less intense optical fields, polarizability is constant giving rise to characteristic optical properties of materials such as the refractive index. Changes in polarizability constitute a nonlinear dependence of electronic polarization with light intensity, and this phenomenon is known as optical nonlinearity. Crystals that exhibit these effects are called nonlinear optical materials (qv).

Nonlinear optical (NLO) and electrooptic (EO) processes are events that take place in transparent materials where refractive indexes can vary with electric field intensity. The field elicits a polarization response in which terms dependent on second and higher orders of the field intensity become significant contributions to the overall polarization response. As light propagates through a transparent solid, liquid, or gas, it encounters the electric fields associated with the valence electrons, polarizing them and creating oscillating electric dipoles. These oscillators in turn act as antennas to broadcast or propagate the electric field through the medium. At low optical intensities, the polarizability P thus induced varies linearly with the electric field E:

$$P_i = \chi_{ij}^{(1)} E_j \qquad (1)$$

where $\chi_{ij}^{(1)}$ is the linear polarizability. As electric field strength increases, eventually the polarization amplitude is no longer able to follow the electric field in a perfectly linear fashion. The polarizability, P_i, must now be expressed as a power series and the higher order terms become more significant with increasing field intensity:

$$P_i = \chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l + \cdots \qquad (2)$$

NLO effects result when the polarization response of the valence electrons becomes significantly anharmonic, usually in intense light beams where the magnitude of E is very large. The magnitudes of the coefficients of the terms in equation 2 diminish rapidly at higher orders, and thus readily observable NLO effects are either second-order ($\chi^{(2)}$) or third-order ($\chi^{(3)}$) processes. Most NLO applications rely on second-order processes. However, second-order processes generally occur only in crystalline materials that lack centers of inversion symmetry. Certain classes of materials such as piezo-, pyro-, and ferroelectric ceramics are noncentrosymmetric and are thus good candidates for use in constructing NLO devices. In fact, ferroelectric ceramics comprise the bulk of technologically useful nonlinear optical materials (see Ferroelectrics).

1.1. NLO Wavemixing

Second harmonic generation (SHG) can be considered the mixing of two light waves of frequency ω to give a wave of frequency 2ω. It is also known as frequency doubling. This is readily accomplished by passing a beam of laser light through a NLO material appropriate for the wavelength and intensity of the beam. Sum-frequency generation (SFG) results when light waves of different frequencies mix to yield a wave where the frequency is the sum of those of the incident beams, and optical parametric oscillation (OPO) can be viewed as the disproportionation of a single beam into waves where frequencies add up to that of the original beam. These wavemixing processes can be highly efficient; for example, up to 70% of the energy from a 1064 nm Nd:YAG laser beam can be converted into 532 nm light by passing it through a crystal of potassium niobate [12030-85-2], $KNbO_3$, or potassium titanyl phosphate, $KTiOPO_4$.

1.2. Optical Phase Retardation

A static electric field applied to a ceramic changes its refractive indexes unequally, altering its birefringence, ie, the difference between its minimum and maximum refractive indexes. This changes the polarization of a light beam transmitted through the crystal by altering the phase angle by which light polarized in the plane of the optic axis (the *e*-ray) leads or lags light polarized normal to the optic axis (the *o*-ray). Such an electrooptic (EO) device acts as a variable phase retarder, and can modulate either the frequency or the amplitude of a transmitted beam. Lithium niobate [12031-63-9], $LiNbO_3$, and lead lanthanum zirconate titanate (PLZT), $(Pb,La)(Zr,Ti)O_3$, are ceramic materials frequently used for EO applications.

1.3. Photorefractive Effect

In certain crystals, such as barium titanate [12047-27-7], $BaTiO_3$, and strontium barium niobate (SBN), $Sr_{1-x}Ba_xNb_2O_6$, applying a light pattern that causes alternate portions of the crystal to become illuminated or dark, eg, from the interference of two light beams, causes photoexcited charge carriers to drift from the illuminated to the dark regions, where they are trapped. This results in space charge fields in the crystal, which in turn causes adjacent zones to have different refractive indexes, setting up a diffraction grating within the crystal. Once written, this pattern can remain in the crystal for a considerable length of time until it is erased by strong, uniform illumination. This grating can diffract subsequent beams and is thus capable of storing, processing, and amplifying complex optical information such as images (see Holography).

2. Materials and Processing

2.1. Materials

NLO materials possess a high degree of optical nonlinearity, physical durability and chemical inertness, and high threshold to optical damage. In addition, it must be possible to process the materials into the form required by the intended application.

Optically nonlinear ceramics all contain highly polarizable bonds. In the case of oxide ceramics, such polarizable bonds are often found between oxygen and early transition metals, eg, $BaTiO_3$, $SrNb_2O_6$, and $KTaO_3$; boron, eg, LiB_3O_5, β-BaB_2O_4; the heavy *p*-block elements, eg, TeO_2, HIO_3, $Pb_3(PO_4)_2$, and $Bi_{12}SiO_{20}$, and in compounds containing tetrahedral XO_4 groups, eg, $KLiSO_4$, KH_2PO_4, and $Gd_2(MoO_4)_3$. These compounds must crystallize in structures that favor highly directional bonding in order to yield good optical nonlinearities. For example, in $LiNbO_3$ the niobium atoms are not centrally located on six-coordinate (octahedral) positions but are off-center, rendering three niobium–oxygen bonds shorter than the others. The extra electron density within these short bonds causes them to become unusually polarizable. As in the bulk crystal, the polarizability of the Nb–O bonds contains higher order terms that result from anharmonicity in their electronic potentials. The first higher order term, β_{ijk}, is a microscopic susceptibility tensor that relates the second-order susceptibility of a bond or group to the bulk tensor $\chi^{(2)}_{ijk}$:

$$\chi^{(2)}_{ijk} = NG_{ijk}\beta_{ijk} \qquad (3)$$

Here N is the number of bonds or molecules of a given type in the crystal, and G_{ijk} is a geometric tensor associated with a particular microscopic polarizability β; this tensor is related to the crystallographic orientation of the bond. In extended systems such as covalent solids it becomes difficult to define a species to which one can assign a unique value of β, and thus the value of β for a given group can only be an approximate representation. In lithium niobate the short, highly polarizable bonds align to give a nonzero value of β_{ijk} for the NbO_6 group. The β_{ijk} tensor is repeated in the same direction in each crystallographically equivalent group throughout the crystal, resulting in a large value of $\chi^{(2)}$. In contrast, the Ti atoms in cubic $BaTiO_3$ $(\mathrm{T} > 120^{\circ}\mathrm{C})$ are centered in their respective octahedral sites, and the polarizabilities of the Ti–O bonds yield a net value of zero for the β_{ijk} terms of the TiO_6 groups.

Nonoxide NLO ceramics include Si and compound semiconductors (qv) having the silicon structure, eg, GaAs, InP, and InSb, as well as ferroelectrics such as SbSI. These materials tend to be more highly nonlinear than oxide ceramics, although lack of transparency at visible and uv wavelengths prevents them from competing with the oxides for the same applications.

Second-order nonlinearity in ceramics can also be seen as arising from a mixing of states in which the ground state can partially acquire the character of an excited state with a strong dipole moment, eg, a charge-transfer band or conduction band. The degree of optical nonlinearity that results depends on the extent to which the excited state is delocalized, as in the case of a conduction band, and the energy difference between the ground and excited states, that is, the band gap. Nonlinear susceptibilities of the best materials at a given wavelength tend to vary inversely with band gap.

NLO ceramics frequently used in the visible-near ir region generally crystallize in ferroelectric structure types, such as $LiNbO_3$ and the perovskite, eg, $KNbO_3$, $BaTiO_3$; tungsten bronze, eg, $BaNa_2Nb_5O_{15}$, $Sr_{1-x}Ba_xNb_2O_6$; KH_2PO_4; and $KTiOPO_4$ structures (see Infrared and raman spectroscopy). Compounds with smaller nonlinearities but wider transparency regions include lithium borate, (LBO), LiB_3O_5, and β-barium borate (BBO), β-BaB_2O_4. The latter can frequency mix to wavelengths as short as 213 nm.

The physical durability of bulk ceramics and their resistance to chemical attack under ambient conditions allow device fabrication and use. Ceramics are generally resistant to optical damage, although damage thresholds can vary widely. Optical damage can result from thermal breakdown, in which prolonged illumination results in excessive heat build-up, usually in devices pumped by continuous-wave lasers, and avalanche breakdown, in which the electric field induced within the ceramic by the light beam exceeds the dielectric strength of the material, usually in high power pulsed-beam applications. Avalanche breakdown, which is often accompanied by a flash of broadband light resembling a spark, can cause dark inclusions to appear in the crystal. These introduce absorption and render the crystal more susceptible to further damage. Point defects such as vacancies and metal atom impurities in ceramics can lower the power threshold to avalanche breakdown, which in turn lowers the maximum useful laser power that may be safely used with the ceramic, limiting its efficiency.

2.2. Processing

All-optical wavemixing applications generally require single crystals. The crystals should have relatively low concentrations of point defects, which have been implicated in low thresholds to optical damage. Typical defects in ferroelectrics include Schottky defects and nonstoichiometry, which result in ions residing on the wrong crystallographic positions, eg, siting Nb on Li positions in $LiNbO_3$.

If the ceramic of interest melts congruently, eg, $LiNbO_3$ and $BaTiO_3$, crystals can be grown using the Czochralski method. In this technique a seed crystal suspended from a rotating mount is slowly withdrawn from a melt causing the material on the seed to crystallize as its temperature falls below the melting point. Eventually a large boule is pulled from the melt, from which crystals may be cut. If the ceramic melts incongruently, eg, $KTiOPO_4$, or is a phase not stable at the composition's melting point, eg, SiO_2, crystals may sometimes be grown hydrothermally, or from a nonaqueous flux.

In the flux-growth method, crystals of the desired ceramic are precipitated from a melt containing the components of the product phase, often in addition to additives used to suppress the melting point of the flux. These additives remain in solution after crystal growth is complete. Crystals are precipitated onto seeds by slowly cooling the melt or the seed, or occasionally by evaporating volatile components of the melt such as alkali halides, depressing the solubility of the product phase.

In the hydrothermal method, crystals of the desired ceramic are grown by dissolving the product or nutrient in the form of powder or small crystals in an aqueous solution of a mineralizer, which enhances the solubility of the nutrient. Examples of mineralizers include NaOH and K_2HPO_4, which aid the solution of SiO_2 (quartz) and $KTiOPO_4$, respectively. Crystal growth takes place in an autoclave that is heated above the critical temperature of water (374°C) and pressurized to maintain a density sufficient for adequate nutrient solubility. The disadvantages of greater equipment complexity and cost are often outweighed by the lower viscosity of the supercritical flux, which reduces flux inclusion, and lower growth temperatures that often yield lower defect concentrations.

3. Techniques and Applications

3.1. Frequency Conversion

SHG is most often used to double the frequencies of solid-state and diode lasers operating in the near infrared to yield an output beam in the visible spectrum. In this process laser light, frequently from a pulsed solid-state laser such as Nd:YAG, is directed through a doubling crystal such as LiB_3O_5 (LBO), KH_2PO_4 (KDP), etc in a direction that allows the output beam to remain in phase with the input beam. The emerging beam contains light at both the incident (fundamental) and second harmonic (SH) wavelengths. The extent to which light energy is converted to energy at this second harmonic (SH) frequency depends on the magnitudes of the coefficients of the $\chi^{(2)}$ tensor (eq. 2), as well as intensity of the fundamental beam. The chief material requirements for SHG are therefore high NLO coefficients and a high optical damage threshold. Other important criteria include optical transparency in the wavelength range of interest, and the ability to phase match the fundamental and SH beams. For phase matching to occur, there must be some angle of incidence through the crystal for which both the fundamental and second harmonic waves experience the same phase velocities, so that the velocity v_p of the SH wavevector k equals that of the fundamental wavevectors. Normal dispersion makes this a special condition: the crystal must be optically anisotropic, either uniaxial or biaxial, and the birefringence of the crystal must be such that the refractive indexes experienced by the interacting waves as they propagate through the medium match, ie $n(\omega) = n(2\omega)$, at some point on the surface of the refractive index ellipsoid (Fig. 1**a**). The refractive index ellipsoid defines n_i for a given polarization and crystallographic direction of propagation. If the refractive indexes do not match, the fundamental and SH beams cannot propagate in phase with one another. The distance the beams must propagate through the crystal to change the phase difference in the two beams is the coherence length l_c, which equals $\lambda/4(n_{2\omega}-n_\omega)$. The coherence length for a perfectly phase matched crystal is thus infinite.

Biaxial crystals offer the possibility of coincidence of the phase matching direction with one of the optic axes. This highly desirable situation, called non-critical phase matching, is quite tolerant of divergence of the incident beam from the most efficient phase matching direction.

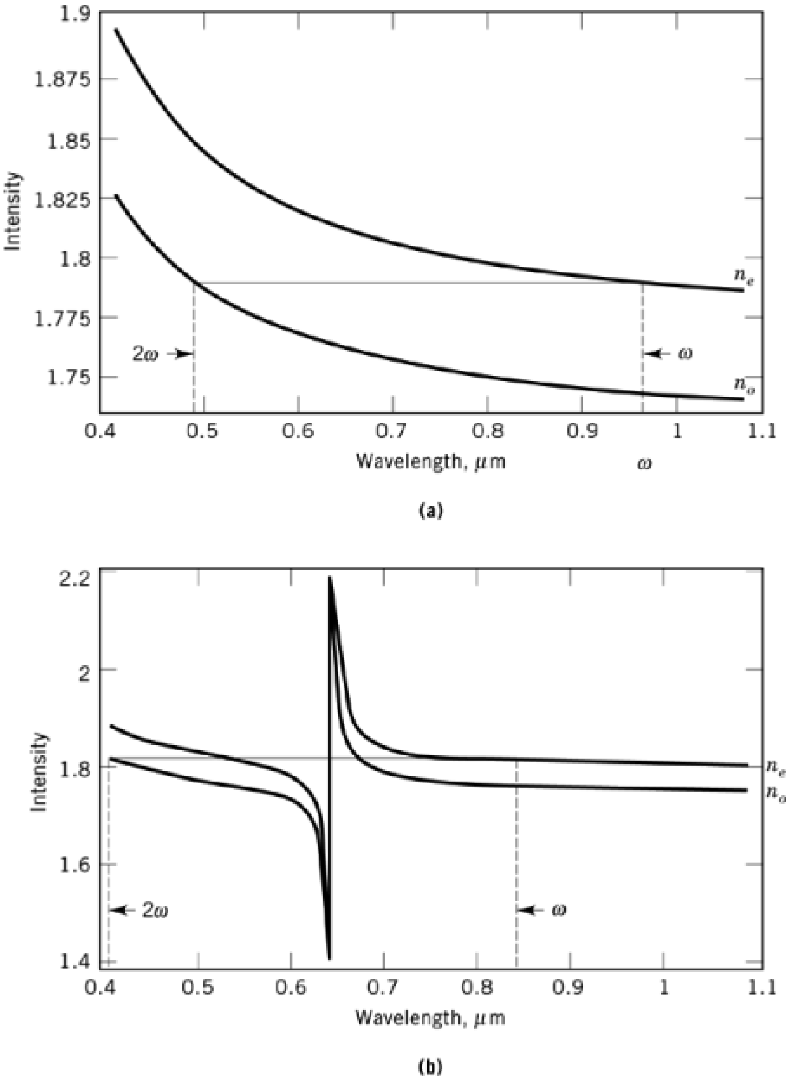

Fig. 1. (**a**) Phase matched second harmonic generation ($2\omega=0.49\ \mu\mathrm{m}$) at $\omega=0.98\ \mu\mathrm{m}$, where n_0=refractive index by ordinary rays and n_e=by extraordinary rays. (**b**) Hypothetical anomalous dispersion phase matching at 850 nm in similar a crystal having a Lorentzian absorption centered at 650 nm.

Anomalous dispersion offers another method of phase matching. Anomalous dispersion, the opposite of normal dispersion, refers to a decrease in refractive index with decreasing wavelength and is associated with optical absorption. The magnitude of anomalous dispersion depends on the width and intensity of the absorption band. In principle, it is possible to introduce absorption between fundamental and SH wavelengths to reduce or overcome normal dispersion, allowing phase matching to take place in a weakly birefringent crystal (Fig. **1b**). As of this writing, anomalous dispersion-assisted phase matching has not been demonstrated in inorganic crystals.

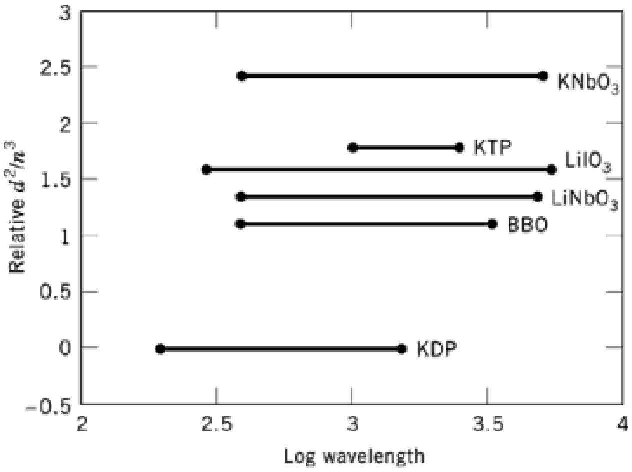

Fig. 2. Optical nonlinearity and phase matching windows for commonly used NLO materials. KDP=KH_2PO_4; BBO=$\beta-BaB_2O_4$; KTP=$KTiOPO_4$. Wavelength is in units of nm. d^2/n^3=normalized second order susceptibility with refractive index.

The range of useful SHG wavelengths for a given material is usually marked by the limits of its phase matching ability, as this window is usually narrower than its transparency range. Phase matching ranges and NLO coefficients for some of the more familiar NLO materials are given in Figure 2.

SH light can be used to pump a second NLO crystal to generate light at one-third the wavelength of the fundamental (cascade tripling) through sum-frequency generation (SFG), to yield a wavelength-tunable output beam through optical parametric oscillation (OPO), to drive a dye laser or Raman shifter, or in optical data storage (see Information storage materials).

3.2. Electrooptic Devices

Electrooptic (EO) materials are optical media in which birefringence can be readily induced or altered by an externally applied electric field. Birefringence, which is the difference between minimum and maximum refractive index (Δn) in an optical medium, occurs in anisotropic crystals, stressed glasses, poled ceramics, or any transparent medium subjected to an external electric field. If linearly polarized light enters a birefringent material normal to its optic axis, the maximum attenuation obtained from an analyzer is found when the analyzer is offset from 90° by a certain phase retardation angle. This phase retardation angle depends on the birefringence and thickness of the element, and on the wavelength of light being transmitted.

The incident beam is broken up into an ordinary ray (*o*-ray) polarized normal to the optic axis, and an extraordinary ray (*e*-ray) polarized in the plane of the optic axis. The extraordinary ray is so named because unlike the ordinary ray, it does not obey Snell's law of refraction. The *o*-ray and the *e*-ray experience different refractive indexes and therefore different phase velocities. Either the *o*-ray or the *e*-ray lags behind the other in phase and the emerging beam is elliptically polarized. The sign of the birefringence determines which ray is retarded: in a positive uniaxial crystal, the optic axis is a fast axis and the *o*-ray leads in phase; conversely, if the birefringence is negative the optic axis is the slow axis and the *o*-ray lags behind the *e*-ray. The phase retardation Γ experienced by the light beam on passing through the optical element is defined as

$$\Gamma = 2\pi L\ (n_o - n_e)/\lambda \qquad (4)$$

where L is the optical path length, n_o and n_e are the refractive indexes experienced by the *o*-ray and *e* ray, and λ is the wavelength of the incident beam. If $\Gamma = \pi/2$ the emerging beam is circularly polarized and the element is a quarter-wave plate. If $\Gamma = \pi$, the beam is linearly polarized orthogonally to the polarization of the incident beam, and the element is a half-wave plate. If such a device is placed between two crossed polarizers and rotated, the relative intensity I/Io of light transmitted through this device varies as $\sin^2(\Gamma/2)$.

In an electrooptic material the phase retardation angle is controlled by altering birefringence, which is in turn controlled by the potential of an applied electric field. An electrooptic device thus acts as a variable phase optical retardation plate, and can be used to modulate the wavelength or intensity of an incident beam.

EO effects can be linear or quadratic, depending on whether the degree of phase retardation varies with either the first or second power of applied voltage. The variation of birefringence with potential takes the form

$$r_c = -(2\Delta n)/n^3E \qquad (5)$$

where r_c is the linear, or Pockels, coefficient and

$$R = -(2\Delta n)/n^3E^2 \qquad (6)$$

where R is the quadratic or Kerr coefficient. As is the case with second-order NLO materials, phases demonstrating the Pockels effect are noncentrosymmetric, though no such constraint is placed on materials demonstrating the Kerr effect. In general, large values of r_c and R for a given material correlate with increased $\chi^{(2)}$ and $\chi^{(3)}$ effects at optical frequencies.

As with NLO ceramics, good EO materials tend to be ferroelectrics. Ferroelectric materials are noncentrosymmetric, allowing one to take advantage of the linear response and increased magnitude of the Pockels effect vs the Kerr effect. Also, the large low frequency dielectric constants typical of many ferroelectric ceramics are conducive to high values of r_c, although larger dielectric constants necessitate a higher driving voltage to achieve a given response. EO ceramics are also frequently based on perovskite and tungsten bronze structures containing Nb and Ti, and include $LiNbO_3$, $PbZr_{1-x}Ti_xO_3$ (PZT), $KTiOPO_4$, $Sr_{1-x}Ba_xNb_2O_6$, $Ba_2NaNb_5O_{15}$, and $BaTiO_3$.

Inorganic electrooptic materials can take the form of single crystals or polycrystalline ceramics. For certain applications such as switching and interferometry, single crystals carry certain advantages over polycrystalline compacts. On the other hand, polycrystalline ceramics can be hot-pressed or sintered into a larger variety of shapes and sizes, without regard to crystallographic orientation. In addition, the orientation of the optic axis in such polycrystalline ceramic elements can be controlled by the external electric field. It should be noted that operations making use of properties that depend on crystallographic orientation, such as SHG, would be difficult to accomplish with pressed ceramics consisting of randomly oriented crystallites.

EO materials are generally used as either bulk optical elements or guided wave devices. Bulk elements are frequently made of polycrystalline ceramics such as lead lanthanum zirconate titanate (PLZT), $(Pb,La)(Zr,Ti)O_3$, whereas guided wave devices are usually fabricated on single crystals of materials such as $LiNbO_3$ and $KTiOPO_4$. Bulk elements are used where significant apertures are required and large modulator bandwidths are less important, and are used in devices such as variable density filters, variable color filters, electrooptic shutters, and as Q-switches for pulsed lasers. The Q-switchtakes advantage of the fast response time of the EO material, admitting a single laser pulse by switching between on and off states in less than 1 ns. Guided wave devices are used as signal modulators and as interferometers. A simple example of such a device is a single channel phase modulator, which alters the phase retardation of a beam propagating through the waveguide. A difference in refractive index between the waveguide and the remainder of the crystal keeps the light beam from escaping the channel. This refractive index gradient is created by replacing metal ions in the crystal with foreign ions through diffusion, eg Ti for Nb in $LiNbO_3$ and Tl for K in $KTiOPO_4$. Such an element can be used to modulate optical phase at very high frequencies, allowing high bandwidth signal transmission through fiber optic cables.

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