A theoretical study of the refractive index of KDP crystal doped with TiO$_2$ nanoparticles

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ABSTRACT

In the present chapter we study a nonlinear response of an optical matrix formed by the K$_2$HPO$_4$ crystal doped with TiO$_2$ nanoparticles. Such doped matrix is a nonlinear optical system that is characterized by the cubic non-linear optical response at picosecond laser pulses. Laser pulses release photoelectrons from nanoparticles, which emerge as free carriers on the nanoparticles’ surface generating an electric field in local area of the K$_2$HPO$_4$ matrix, which results in the phase transition from the paraphrase to the ferroelectric phase state. The appeared ferroelectric phase induces a large polarization around TiO$_2$ nanoparticles, which in turn immediately produces a nonlinear optical response to the laser pulse of the inverse sign, such that the laser beam becomes more focused. The gigantic non-linear susceptibility $\chi^{(3)}$ responsible for the phenomenon of focusing of the laser beam is calculated by using the pseudospin model for the description of ferroelectric crystals and the expressions for nonlinear-susceptibility tensor components computed by other researchers.

Key words: K$_2$HPO$_4$ crystal, ferroelectrics phase transition, TiO$_2$ anatase modification, polarization, refractive index, third-order nonlinear susceptibility, active third-harmonic generation medium

INTRODUCTION

The third-order nonlinear optical effects (including nonlinear absorption and refraction) break the diffraction limit and form superresolution nanoscale spot (Wei, 2015). Especially important are the characteristics of the third-order effects. When a light beam with a frequency of $\omega$ is incident on the isotropic nonlinear medium, the nonlinear effect occurs, and the second-order nonlinear susceptibility $\chi^{(2)}$ can be neglected. The whole polarization is presented as

$$P[E(\omega)] = P^{(1)} + P^{(3)} = \varepsilon_0 \left[ \chi^{(1)} + 3\chi^{(3)} |E(\omega)|^2 \right]E(\omega),$$

where $P^{(1)}$ and $P^{(3)}$ the linear and third-order nonlinear polarization, respectively, and, correspondently, they are provided with the linear $\chi^{(1)}$ and third-order nonlinear $\chi^{(3)}$ susceptibility.
The single crystal potassium dihydrogen phosphate KH₂PO₄ is characterized by a unique set of properties, such as a wide range of optical transparency, nonlinear, electrooptical and piezoelectric effects. However, one of the main weaknesses of the crustal is its relatively low quadratic susceptibility. A possible way to increase the susceptibility and, subsequently, the efficiency of the three-wave processes is by altering its structure through a formation of nanocomposite medium (Grachev et al., 2012; Gayvoronsky et al., 2012, 2013). Nanoparticles incorporation into the KH₂PO₄ matrix was realized in order to design a novel lasing medium, which could result in the appearance of third-order nonlinear $\chi^{(3)}$ susceptibility. One of such nanoparticles is titanium dioxide TiO₂ especially in the anatase phase.

A successful growth of high quality KH₂PO₄ (KDP) crystals with incorporated TiO₂ anatase nanoparticles was demonstrated by Grachev et al. (2012). Those doped crystals of KH₂PO₄ were studied by using transmission and scanning electron microscopy, energy dispersive X-ray analysis, Fourier transformation infrared spectra, electron paramagnetic resonance spectra, and nonlinear optics. It was revealed that TiO₂ nanoparticles are embedded in the KH₂PO₄ not chaotically, but as layers separated at a distance of about 15 µm.

As Grachev et al. (2012) and Gayvoronsky et al. (2012, 2013) shown, the incorporation of anatase nanoparticles into the KH₂PO₄ crystal changes the sign of the refractive nonlinear optical response relatively to that of the pure KH₂PO₄ crystal matrix. The phenomenon is associated with the overlapping of the energy states of intrinsic defects in the crystal matrix and the surface state of TiO₂ nanoparticles.

TiO₂ nanoparticles with an average diameter $2R = 15$ nm are uniformly distributed in plains of the KH₂PO₄ crystal. The density of TiO₂ in the KH₂PO₄ crystal varies from $10^{16}$ to $10^{17}$ m⁻³. This allows one to determine an average distance between these nanoparticles equal to 15 µm in each plain of the KH₂PO₄.

Zamponi, Rothhardt et al. (2012) and Zamponi, Stingl et al. (2012) demonstrated that illumination of the K₂HPO₄ crystal with sub-50 fs pulses centered at a photon energy of 4.5 eV (wavelength 266 nm) excites the motion of ions, which results in the charge relocations induced by electronic excitations via the two-photon absorption. In the electronically excited state of the crystal low-frequency oscillations of the PO₄ tetrahedral have to be coherent, while the average atomic positions remain unchanged. Coherent longitudinal optical and transverse optical phonons, whose motion is dephased on a time scale of several picoseconds, drive the charge relocation generating a soft (transverse optical) mode that triggers a phase transition between the para- and ferroelectric phase of KH₂PO₄.

However, the observed phenomenon still was not studied theoretically. Namely, the mechanism of influence of TiO₂ nanoparticles at passing laser pulses remained unclear. In the present chapter a mechanics of nonlinear changes of the refractive index of the KH₂PO₄ crystal doped with TiO₂ nanoparticles, which were revealed by Gayvoronsky et al. (2012, 2013), Grachev et al. (2012), Zamponi, Rothhardt et al. (2012) and Zamponi, Stingl et al. (2012), is suggested.

**A MECHANISM OF NONLINEAR CHANGES OF THE REFRACTIVE INDEX**

A laser pulse of duration 40 ps passing through the doped KH₂PO₄ crystal (Fig. 1) shows a change in its polarization, which means that anatase nanoparticles affected by the pulse, polarize the KH₂PO₄ crystal and this polarization in its turn affects the laser beam. Moreover, the laser beam seems induces a ferroelectric phase in the KH₂PO₄ even at a room temperature. Is such mechanism possible?

Let us recall the major properties of the crystal KH₃PO₄ (see, e.g. Grindlay, 1970). The crystal has the simplest macroscopic behavior of all the ferroelectrics. The only phase transition occurs at a 122 K; so above this temperature the crystal is in a paraelectric phase with tetragonal symmetry 42m and below in a ferroelectric phase with orthorhombic symmetry mm2. The magnitude of the spontaneous polarization $P^{(0)}$ increases rapidly from zero at the Curie point and saturates or reaches a temperature independent value some 20 degrees below this point. In the paraelectric phase of the crystal the zero
stress and zero electric field values of any compliance matrix display point group symmetry $\overline{4}2m$. These matrices contain twenty-eight non-vanishing elements described by thirteen independent functions of temperature.

A laser pulse in which the electric field reaches the value of $10^8 \text{ V} \cdot \text{m}^{-1}$, which has been demonstrated by Grachev et al. (2012), is able to release $n = 1 - 10^4$ electrons from one nanoparticle, which are distributed around the surface of the droplet. The relaxation time of such excited state of the droplet is about 100 ps. To the moment of relaxation the released electrons induce an electric field

$$E_{\text{particle}} = \frac{n e}{4\pi \varepsilon_0 \varepsilon r^2}$$

around TiO$_2$ nanoparticles in the KH$_2$PO$_4$ crystal, where one can put in the case of an optical light the dielectric constant of the KH$_2$PO$_4$ crystal $\varepsilon = 1$.

The diameter of the laser beam is 1 mm, the length of the KH$_2$PO$_4$ crystal, which passes the pulse, is 1 cm. Having known the volume of the crystal illuminated by the beam and the density of TiO$_2$ nanoparticles, we can estimate the number of such particles in the crystal: $N_{\text{part}} \approx 10^8$.

The power of the pulse was $10^{-5} \text{ J}$, the energy of a photon was 1.17 eV. This allows one to evaluate a number of photons in the pulse: $N_{\text{ph}} \approx 10^{14}$.

The behavior of scattering optical fields by small particles in a 3D-matrix is widely studied in the literature (see, e.g. Venger et al. (1999) and Shen (1989)). Falling optical wave polarizes embedded particles, so that the 3D-matrix (a two-phase heterogeneous system) illuminated with light is characterized by a combination of two permittivities, $\varepsilon_1$ and $\varepsilon_2$. This is a typical case for the Maxwell-Garnett approximation: the KH$_2$PO$_4$ medium is described by a permittivity $\varepsilon_1$ and TiO$_2$ inclusions together with a surrounding local volume of the KH$_2$PO$_4$ matrix are characterized by a permittivity $\varepsilon_2$.

A TiO$_2$ nanoparticle absorbing a photon generates an electric field (1) around it in the KH$_2$PO$_4$ matrix. This electric field is able to transform the local volume of the crystal to the ferroelectric phase. Let us examine the appropriate mechanism.

In the presence of an electric field $E_i$ in the $i$th site of the crystal lattice, the Hamiltonian of the

KH₂PO₄ crystal in the pseudospin presentation looks as follows (Blinc & Žekš, 1975)

\[ H = -\Omega \sum_i S_i^z - \frac{1}{2} \sum_{ij} J_{ij} S_i^z S_j^z - 2\mu \sum_i E_i(t) S_i^x \]  

(2)

where \( S_i^z \) and \( S_j^z \) are components of the pseudospin; \( \Omega \) is the tunneling integral, which for the KH₂PO₄ crystal is equal to approximately 287.7 K (or 200 cm⁻¹); \( J_{ij} \) is the parameter of mutual interaction of the \( i \)th and \( j \)th sites; \( \mu \) is the dipole moment of the \( i \)th site.

Here, in the Hamiltonian (2) the \( z \)-component of the pseudospin sets the operator of dipole moment; the \( x \)-component is the operator of tunneling. The expectation \( S_i^z \) characterizes the difference between the population of the left and right equilibrium positions of hydrogen and the expectation \( S_i^x \) describes the difference in the settling of symmetric and antisymmetric states.

In the midfield approximation the equation for the order parameter has the form

\[ \langle S^z \rangle = \frac{\langle S^z \rangle J_0 + 2\mu E / k_B}{\sqrt{\Omega^2 + \langle S^z \rangle J_0^2}} \tanh \frac{\Omega^2 + \langle S^z \rangle J_0^2}{2T} \]  

(3)

where \( J_0 = \sum_{ij} J_{ij} \langle S_i^z \rangle \). Usually an applied electric field does not influence the order parameter \( \langle S^z \rangle \) and the term \( 2\mu E \) is abandoned, which allows one to obtain from Eq. (3) an equation for the critical temperature \( T_c \) of the transition from ferro- to paraphase

\[ 2\Omega / J_0 = \tanh \left[ \Omega / (2T_c) \right]. \]  

(4)

By the estimate of de Gennes (1963), the parameter \( J_0 = 420 \) K (or 292 cm⁻¹) and the critical temperature is \( T_c = 122 \) K.

An analysis shows that Eq. (3) can be simplified

\[ \langle S^z \rangle = \frac{\mu E / k_B}{2\Omega - J_0} \tanh \frac{\Omega}{2T} \]  

(5)

for a wide range of values of \( E \), from very small and up to about \( 10^9 \) V·m⁻¹, even in the paraphase at a room temperature.

Putting \( \mu = 0.5 \times 10^{-29} \) C·m, we can consider numerical solutions to Eq. (5) for the order parameter \( \langle S^z \rangle \). As follows from expression (1), when only one electron is excited in an anatase nanoparticle, it induces an electric field \( E \sim 10^7 \) V·m⁻¹ at a distance of 10 nm from the nanoparticle and the value of the order parameter \( \langle S^z \rangle \sim 10^{-2} \); \( E \sim 10^6 \) V·m⁻¹ at about 0.1 μm and \( \langle S^z \rangle \sim 10^{-4} \); at larger distances from the nanoparticle in question \( E \) and \( \langle S^z \rangle \) are much smaller and can be abandoned.

In regions with the order parameter the KH₂PO₄ matrix is specified by a spontaneous polarization \( P = 2N_e \mu \langle S^z \rangle \). Therefore, these regions represent ferroelectric domains, though they different from
the classical ferroelectric phase of the KH$_2$PO$_4$ crystal below 122 K. The conventional KH$_2$PO$_4$
ferroelectric phase is specified by the orthorhombic symmetry; in a paraphase the crystal is
characterized by the tetragonal symmetry (Grindlay, 1970; Blinc & Zekš, 1975). Domains in which
$\langle S^2 \rangle \neq 0$ are formed under the applied field $E$ from the paraphase and hence they should remain in
the same tetragonal symmetry (with the presence of $E$, equations (3) and (5) cannot be reduced to Eq. (4)).

The volume of a sphere of the KH$_2$PO$_4$ matrix with a radius 0.1 µm polarized by a TiO$_2$
nanoparticle is around $10^{-20}$ m$^3$; the total volume of such spheres is $V_{\text{tot,part.}} \approx 10^{-12}$ m$^3$, as the number
of TiO$_2$ particles in the system studied is $N_{\text{part}} \approx 10^8$. The volume of the KH$_2$PO$_4$ crystal illuminated
by a laser pulse is $V_{\text{crystal}} = 7.85 \times 10^{-9}$ m$^3$. This allows us to introduce a dimensionless factor
$f_2 = 1.3 \times 10^{-4}$ defined as a ratio of these two volumes, $f_2 = V_{\text{tot,part.}} / V_{\text{crystal}}$. Venger et al. (1999)
suggested the following expression for an effective dielectric function of the heterogenic matrix

$$\tilde{\varepsilon} = \varepsilon_1 \left(1 + \frac{3f_2 \alpha^*}{1 - f_2 \alpha^*}\right), \quad (6)$$

where $\alpha^* = (\varepsilon_2 - \varepsilon_1) / (\varepsilon_2 + 2\varepsilon_1)$ is the normalized dimensionless polarization of the ferroelectric
sphere around a TiO$_2$ nanoparticle.

As demonstrated by Venger et al. (1999), the dielectric susceptibility of each component depends
on the intensity of an applied field $E$,

$$\varepsilon_{\text{non-linear},j} = \varepsilon_j + \chi_j^{(3)} |E|^2 \quad (7)$$

where $j = 1, 2$ and $\chi_j^{(3)}$ is the third-order nonlinear susceptibility of the $i$th component.

An effective third-order nonlinear susceptibility of this double component system by Venger et
al. (1999) is

$$\tilde{\chi}^{(3)} = 81f_2 \chi_2^{(3)} \left[\varepsilon_1 / (\varepsilon_2 + 2\varepsilon_1)\right]^2 \left[\varepsilon_1 / (\varepsilon_2 + 2\varepsilon_1)\right]^2 \quad (8)$$

In ferroelectric crystals calculations of nonlinear-susceptibility tensor components were carried
out by Osman et al. (1998) and Murgan et al. (2002). In particular, detailed expressions for the third-
order coefficients $\chi^{(3)}$ were calculated by Murgan et al. (2002): The authors started from the free
energy $F_0$ per unit volume for cubic symmetry. Passing to other crystal symmetries, such as
tetragonal, orthorhombic and rhombohedral is reached by an introduction of a correction $\Delta F$ to the
free energy, which is small in comparison with the major term $F_0$. Therefore in the first
approximation we may try to apply the results of Murgan et al. (2002) for a theoretical evaluation of
third-order coefficients $\chi^{(3)}$ in the artificially induced ferroelectric phase of the KH$_2$PO$_4$ crystal
doped with TiO$_2$ nanoparticles.

In the case of intensity-dependent refractive index the result for the $x$- and $y$-component of
nonlinear-susceptibility tensor for the tetragonal symmetry of the ferroelectric phase (the KH$_2$PO$_4$
possesses this symmetry at a room temperature) was derived by Murgan et al. (2002)
\[
\chi^{(3)} = \left| \sigma(\omega) \right|^2 \sigma^2(\omega) \left[ \frac{2\beta_2 \epsilon_0^2 s(0)}{\epsilon_0^2} - \beta_1 \right].
\]

(9)

Here, in expression (9), the parameters have been defined by Murgan et al. (2002). In the case of oscillatory dynamics, expression (9) consists of two parts, real and imaginary; the real one can be approximated as follows

\[
\text{Re} \chi^{(3)} \approx \frac{\epsilon_0}{(1 - \beta_2 / \beta_1)^4} \left( \beta_2^2 / \beta_1 - \beta_1 \right)
\]

(10)

The expression (10) should be equated to the parameter \( \chi_2^{(3)} \) in the susceptibility (8). Then having known the parameters \( f_2, \epsilon_1, \epsilon_2, \alpha, \beta_1 \) and \( \beta_2 \), we may calculate the effective third-order harmonic \( \widetilde{\chi}^{(3)} \) of the susceptibility (8).

As was shown experimentally by Colla et al. (1997), KH2PO4 nanosize particles have a significant shift of the transition temperature from the bulk value 122 K to 160 K and the transition broadening; the position of the maximum of the permittivity \( \varepsilon(T) \) and its magnitude do not depend on the measurement frequency; at \( T > 190 \) K the permittivity \( \varepsilon(T) \) increases rapidly with temperature displaying a strong frequency dispersion.

We may use these results, because domains of the ferroelectric phase developed in the KH2PO4 matrix around excited TiO2 nanoparticles are similar in size to those real KH2PO4 nanosize particles. In our case ferroelectric domains have a particular characteristic in a sense that the central part of each of them is the source of its inner electric field (inoculated by the exited TiO2 nanoparticle), which creates an additional radial symmetry. It is impossible to determine a real value of the permittivity in such ferroelectric domains, but unambiguously \( \epsilon_2 >> 1 \). At the same time the value of the permittivity for the KH2PO4 matrix at a room temperature is known, \( \epsilon_1 \approx 2.25 \). Therefore, in expression (8) we may put \( [\epsilon_1/(\epsilon_2 + 2\epsilon_1)]^4 \approx (1/2)^4 \). Then combining expressions (8) and (10), i.e. putting \( \chi_2^{(3)} = \text{Re} \chi^{(3)} \), we get the final expression for the real part of non-linear susceptibility

\[
\widetilde{\chi}^{(3)} \approx \frac{81}{16} f_2 \frac{\epsilon_0}{(1 - \beta_2 / \beta_1)^4} \alpha^4 \left( \beta_2^2 / \beta_1 - \beta_1 \right).
\]

(11)

As we mentioned above, ferroelectric domains formed around TiO2 nanoparticles in the KH2PO4 matrix should comply with the tetragonal symmetry. The ferroelectric phase of tetragonal symmetry was examined by Osman et al. (1998), Murgan et al. (2002) and Ibrahim et al. (2011). In particular, it was found by Ibrahim et al. (2011) that the material parameters \( \beta_1 \) and \( \beta_2 \) are related through a simple relationship \( \beta_2 = 3\beta_1 \); besides, the value of \( \beta_1 \) is directly connected to the spontaneous polarization equation

\[
P_s = \epsilon_0 \alpha / \beta_1
\]

(12)
in the tetragonal phase.

Expression (11) includes only one fit dimensionless parameter \( \alpha = a \cdot (T - T_c) \), where by the definition of Murgan et al. (2002) \( a = 1 / C \) and \( C \) is the Curie constant, which remains undetermined. By Samara’s (1973) data for the bulk crystal KH2PO4 \( C = 2925 \) K; hence at room temperature \( \alpha \)

could be equal to $5.91 \times 10^{-2}$. However, the domains in question are formed around TiO₂ nanoparticles that have to influence the local symmetry of the KH₂PO₄ matrix, the more so that a photoelectric excited TiO₂ nanoparticle introduces an additional radial symmetry in its environment (via the Coulomb distribution of the particle’s filed $E_{\text{particle}}(1)$). Such distortions are able to significantly decrease the value of $\alpha$. This should effect the parameters $\beta_1$ and $\beta_2$, as they are very sensitive to the magnitude of the spontaneous polarization $P_s$, which was exhibited by Murgan et al. (2002).

Let us put $\alpha = 6 \times 10^{-4}$. Since for KH₂PO₄ $P_s = 5.1 \times 10^{-2} \text{ C} \cdot \text{m}^{-2}$, as was calculated by Samara (1973), we may immediately calculate from Eq. (12) the parameter $\beta_1$ for our domains: $\beta_1 \approx 1.04 \times 10^{-13} \text{ m}^3 \cdot \text{J}^{-1}$. Then $\beta_2 \approx 3.13 \times 10^{-13} \text{ m}^3 \cdot \text{J}^{-1}$. Substituting these values into expression (11) we finally get in SI:

$$\tilde{\chi}^{(3)} \approx 2.3 \times 10^{-15} \text{ m}^2 \text{ V}^{-2},$$

or in SGS:

$$\tilde{\chi}^{(3)} = \left(9 \times 10^8 / (4\pi)\right) \times 2.3 \times 10^{-15} = 1.6 \times 10^{-7} \text{ cm}^2 \text{ statV}^{-2}. \quad (14)$$

Such a gigantic value of third-order nonlinear susceptibility, which is 5 to 7 orders large than that of the majority of materials that are transparent at the fundamental and third harmonic wavelengths (see, e. g. Thalhammer & Penzkofer, 1983; Leupacher & Penzkofer, 1985; Nasu et al., 1994; Wang et al., 2014) and 3 orders greater than that of the pure crystal KH₂PO₄. The estimated value of $\chi^{(3)}$ (13) exceeds even an effective third-order susceptibility for graphene that is on the order of $10^{-16}$ m² V⁻² (Kumar et al., 2013), which is comparable to that for special materials that are resonantly excited.

The refraction index is defined by the expression

$$n = \sqrt{\frac{|\varepsilon| + \varepsilon_i}{2\varepsilon_o}} \quad (15)$$

where the dielectric function $\varepsilon = \varepsilon^{(1)} + \Delta \varepsilon$. Here, $\varepsilon^{(1)} = \varepsilon_0(1 + \chi^{(1)})$ is the linear dielectric function and $\Delta \varepsilon = 3\varepsilon_0\chi^{(3)} |E|^2$ is the nonlinear contribution to $\varepsilon_0$ due to third-order nonlinear polarization of the matrix KH₂PO₄ that includes TiO₂ nanoparticles. The sign of the parameter $\chi^{(3)}$ (13) and (14) measured by Gayvoronsky et al. (2012, 2013) is negative, which means that the refracted light focuses the laser beam.

**SUMMARY**
Thus we have shown that in the K$_2$HPO$_4$ crystal doped with TiO$_2$ nanoparticles of the anatase modification, intensive laser pulses change the paraphase state of the crystal to the ferroelectric state even at a room temperature. Namely, absorbing a light pulse TiO$_2$ nanoparticles release photoelectric electrons, which in turn generate an electric field that extends into the crystal matrix. This electric field spreads up to a few tens of nanometers from each nanoparticle. The induced electric field is so strong in such local ranges around nanoparticles that is able to transform the matrix paraphase state to the ferroelectric state. The ferroelectric domain emerged around each TiO$_2$ nanoparticle produces a quite strong polarization $P$ that is specified also the third-order nonlinear component provided with the third-order nonlinear $\chi^{(3)}$ susceptibility. Our task has been the calculation of this cubic susceptibility. We have used a typical expression for $\chi^{(3)}$ presented in literature and investigated its parameters by using the appropriate values calculated by other researchers for the pure KH$_2$PO$_4$ crystal and the properties of the derived ferroelectric domain formed around TiO$_2$ nanoparticles in such a matrix. As the result, we have evaluated the value of a giant non-linear optical response, $\chi^{(3)} \sim 10^{-7}$ esu, which is three orders of magnitude greater than that is the case for the response of the pure KH$_2$PO$_4$ crystal being in the paraphase state at a room temperature.

Thus the reason for such a giant non-linear optical response of the KH$_2$PO$_4$ crystal doped with TiO$_2$ nanoparticles is caused by the induction of the ferroelectric domains around these nanoparticles, which occurs even at a room temperature (though at usual conditions the KH$_2$PO$_4$ crystal remains in the ferroelectric state only below the Curie temperature that equals 122 K). Thereby we may conclude that the crystal KH$_2$PO$_4$ doped with TiO$_2$ nanoparticles can be utilized as the most promising active third-harmonic generation medium.

REFERENCES


KEY TERMS AND DEFINITIONS

Anatase: one of the three mineral forms of titanium dioxide TiO2, the other two being brookite and rutile.

Ferroelectricity: a property of certain materials that have a spontaneous electric polarization, i.e. the materials have a permanent electric moment.

Nonlinear optics: describes the behavior of very intensive light in nonlinear media, i.e. media in which the dielectric polarization $P$ responds nonlinearly to the electric field $E$ of the light.

Nonlinear Polarization: the part of the light-induced electric polarization that depends nonlinearly on the electric field $E$ of the light.

Refractive index: the ratio of the velocity of light in a vacuum to its velocity in a specified medium.

Second harmonic generation: generation of light with a doubled frequency (half the wavelength), two photons are fusing creating a single photon at two times the frequency.

Spontaneous polarization: exists within a material in the absence of the application of an external electric field. Usually used in the context of electric fields and electrical polarization. Materials that exhibit spontaneous polarization are piezoelectric that are able to retain an ionic polarization and therefore said to be ferroelectric.

Third harmonic generation: generation of light with a tripled frequency (one-third the wavelength), three photons are transformed forming a single photon at three times the frequency.

Third-order nonlinear susceptibility: the lowest-order nonlinearity, which is generated by a nonlinear medium that possesses a center of symmetry.