Chapter 13

A Theoretical Study of the Refractive Index of KDP Crystal Doped with TiO\textsubscript{2} Nanoparticles

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ABSTRACT

In the present chapter we study a nonlinear response of an optical matrix formed by the K\textsubscript{2}HPO\textsubscript{4} crystal doped with TiO\textsubscript{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\textsubscript{2}HPO\textsubscript{4} matrix, which results in the phase transition from the paraphase to the ferroelectric phase state. The appeared ferroelectric phase induces a large polarization around TiO\textsubscript{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.

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

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

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where $P^{(1)}$ and $P^{(3)}$ the linear and third-order nonlinear polarization, respectively, and, correspondingly, they are provided with the linear $\chi^{(1)}$ and third-order nonlinear $\chi^{(3)}$ susceptibility.

The single crystal potassium dihydrogen phosphate $\text{KH}_2\text{PO}_4$ 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 crystal 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 $\text{KH}_2\text{PO}_4$ 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 $\text{TiO}_2$ especially in the anatase phase.

A successful growth of high quality $\text{KH}_2\text{PO}_4$ (KDP) crystals with incorporated $\text{TiO}_2$ anatase nanoparticles was demonstrated by Grachev et al. (2012). Those doped crystals of $\text{KH}_2\text{PO}_4$ 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 $\text{TiO}_2$ nanoparticles are embedded in the $\text{KH}_2\text{PO}_4$ 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 $\text{KH}_2\text{PO}_4$ crystal changes the sign of the refractive nonlinear optical response relatively to that of the pure $\text{KH}_2\text{PO}_4$ 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 $\text{TiO}_2$ nanoparticles.

$\text{TiO}_2$ nanoparticles with an average diameter $2R=15$ nm are uniformly distributed in plains of the $\text{KH}_2\text{PO}_4$ crystal. The density of $\text{TiO}_2$ in the $\text{KH}_2\text{PO}_4$ 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 $\text{KH}_2\text{PO}_4$.

Zamponi, Rothhardt et al. (2012) and Zamponi, Stingl et al. (2012) demonstrated that illumination of the $\text{K}_2\text{HPO}_4$ 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 $\text{PO}_4$ 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 $\text{KH}_2\text{PO}_4$.

However, the observed phenomenon still was not studied theoretically. Namely, the mechanism of influence of $\text{TiO}_2$ nanoparticles at passing laser pulses remained unclear. In the present chapter a mechanics of nonlinear changes of the refractive index of the $\text{KH}_2\text{PO}_4$ crystal doped with $\text{TiO}_2$ 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 $\text{KH}_2\text{PO}_4$ crystal (Figure 1) shows a change in its polarization, which means that anatase nanoparticles affected by the pulse, polarize the $\text{KH}_2\text{PO}_4$ crystal and this polarization in its turn affects the laser beam. Moreover, the laser beam seems induces a ferroelectric phase in the $\text{KH}_2\text{PO}_4$ even at a room temperature. Is such mechanism possible?