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Influence of gamma radiation on the second-order optical susceptibilities and piezoelectricity of the $Rb_{1-x}K_xTiOPO_4$ single crystals

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We have performed nonlinear optical and piezoelectric studies of the $Rb_{1-x}K_xTiOPO_4$ (RKTP) (with $x = 0.01$ and 0.002) single crystals irradiated by γ-quanta at power 1.23 Gy. We have found that for non-irradiated samples with $x = 0.01$ the effective second-order susceptibilities determined from the powder-like micrometer samples were less than for $x = 0.02$ and the effective values of the second-order susceptibilities for 1064 nm were equal to 3.12 pm/V ($x = 0.002$) and 2.56 pm/V ($x = 0.01$). After the gamma irradiation the corresponding values were equal to 2.45 pm/V and 2.78 pm/V, respectively. Moreover, for the samples with $x = 0.01$ one can observe the occurrence of the damage at laser energy density equal to about several J/cm^2. Such effect is absent for the pure KTP crystals and may be a consequence of substantial role of the intrinsic defects caused by insertion of potassium ions in the positions of the rubidium cations. At the same time the piezoelectrical constants show an opposite behavior with respect to the SHG.

Keywords: nonlinear optical crystal, flux growth, gamma irradiation, second-order susceptibility.

1. Introduction

It is well known that crystals of $KTiOPO_4$ (KTP) family demonstrate excellent second--order optical susceptibilities and first of all are NLO materials for second-harmonic generation applications [1, 2].

KTP is a widely used material for frequency-doubling Nd:YAG lasers and other Nd^{3+}-doped laser systems emitting near 1064 nm. Although a few specific characteristics of other materials are better, KTP has a combination of properties that make it unique for second-order nonlinear-optical applications and second-harmonic generation (SHG) of Nd^{3+} lasers in particular. Its large nonlinear coefficients are phase

matched, resulting in a high figure of merit. This property, combined with low absorption and a wide matched angle, makes it the preferred doubling crystal when the available peak power is limited.

Potassium titanyl phosphate (KTP) is a relatively new material that has been shown to have superior properties for several nonlinear-optical applications and, in particular, for frequency doubling for the 1.06 μm radiation of Nd^{3+} lasers. Because KTP belongs to the space group $Pna2_1$, ferroelectric domains can be present, which decrease nonlinear optical conversion efficiencies. Even though the effective nonlinear coefficient of periodically-poled KTP (PPKTP) crystals is lower than periodically-poled $LiNbO_3$ (PPLN), KTP has still the advantage of being able to operate at room temperature without causing photorefractive damage. Efficient frequency-doubling was demonstrated in PPKTP crystals pumped by high-power pulsed Nd:YAG lasers [3, 4]. KUKLEWICZ *et al*. have utilized a single PPKTP crystal with a single-beam output that can be post-selected by a 50–50 beam splitter to produce a high flux source of polarization-entangled photons [5]. FIORENTINO *et al*. overcome this restriction by using a bidirectional pumping scheme with a single PPKTP crystal that has produced an ultra-bright source of polarization entanglement at the expense of phase locking of the interferometric arrangement [6, 7]. The KTP structure was determined by TORDJMAN *et al.* in 1974 [8]. KTP belongs to the family of compounds that possess the formula unit $MTiOXO_4$, where M are K, Rb, Tl, NH_4, or Cs (partially) and X are P or As. Solid-state solutions exist among the various members of this family, with only slight changes in lattice parameters. All members are orthorhombic and belong

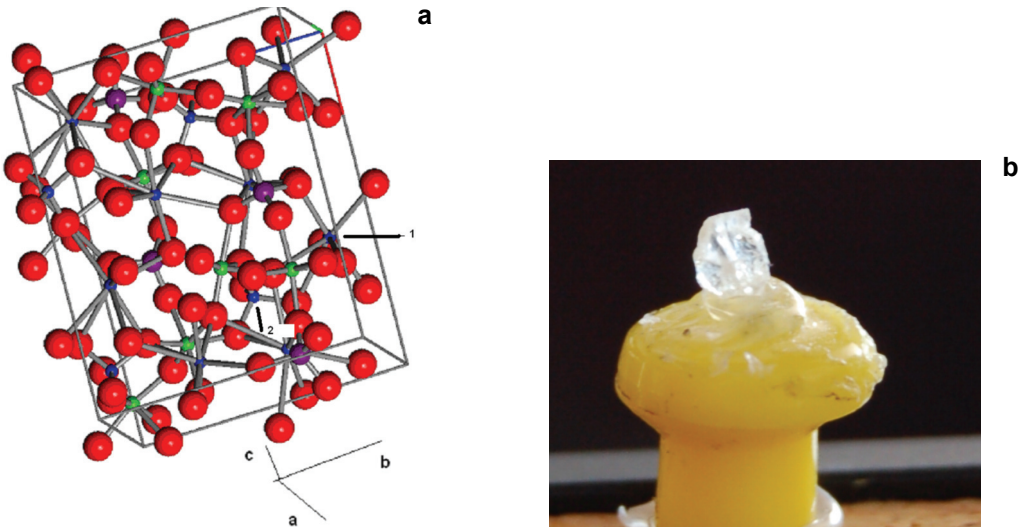

Fig. 1. Projection of the KTP crystal structure: red – oxygen, blue – potassium, green – titanium, violet – phosphorus. The crystallographic axis *c* corresponds to the polar direction. The two positions of the Ti are indicated by 1 and 2 (**a**). The position of the RKTP crystal with respect to the measurement set-up (**b**).

to the noncentrosymmetric point group *mm* (space group $Pna2_1$). For KTP the lattice constants are a = 12.814 Å, b = 6.404 Å, and c = 10.616 Å, and each unit cell contains eight formula units. The structure is characterized by chains of TiO_6 octahedra, which are linked at two corners, and the chains are separated by PO_4 tetrahedra. There are two different types of octahedra. For the first type TiO_6 contains a short Ti–O bond (of approximate length 1.7 Å) and a long Ti–O bond (approximately 2.1 Å) [8], for the second group a short Ti–O bond (of approximate length 1.65 Å) and a long Ti–O bond (approximately 2.21 Å) [9]. The difference in bond length makes the TiO_6 highly distorted. It has been suggested that alternating the long and the short Ti–O bonds will result in a net polarization along the polar axis which is the major contributor to the nonlinear optic coefficient for KTP [9–11]. Figure 1**a** shows KTP crystal structure.

Figure 1**b** presents a photo of the crystal and its positions in the experimental set-up. The $Rb_xK_{1-x}TiOPO_4$ (RKTP) single crystals [1, 12] may be particularly interesting due to the better possibility for poling of such crystals. During last decades, many attempts have been made to improve the properties of KTP family crystals and to develop new applications of KTP for waveguide [13], electrooptic devices [14], periodic poling [15, 16], *etc*. At present, most commercial KTP crystals are grown with the flux method instead of the hydrothermal method. Typical flux-grown KTP crystals are obtained at a temperature around 900 °C, depending on the initial composition. The ionic conductivity of flux-grown KTP is equal to 10^{-6} S/cm range along the polar axis.

KTP doped with Rb is an interesting candidate for periodic poling as we know that both KTP and RKTP can be poled with good results. The reduction of the ionic conductivity for RKTP is a result of the higher activation energy for Rb^+ (0.45 eV) with respect to K (0.33 eV) in the crystal lattice [16]. This is caused by the fact that Rb^+ has a larger atomic radius than K^+ [12].

2. Crystal growth

Incongruently melting RKTP single crystals were grown by spontaneous crystallization from high-temperature solutions in $Rb_6P_4O_{13}$ solvent. The composition of starting melt was 6:10 ($Rb_{1-x}K_xTiOPO_4/Rb_6P_4O_{13}$) in mass ratio. The crystallization was carried out in a platinum crucible covered with a platinum lid, which was placed in a low temperature gradient two-zone resistance furnace. The temperature of the heating zones was stabilized independently by two 906S Eurotherm controllers. To assure full dissolution of the components the melt was soaked for 24 hours at 950 °C and then relatively quickly cooled to 900°C, when crystallization started. From that point the temperature was lowered at a rate of 1 K/h. The crystallization took two weeks and after that time the furnace was cooled to room temperature at a rate of 20 K/h. The as-grown RKTP single crystals were extracted from the solidified melt with the use of hot water.

3. Gamma-quanta irradiation

Irradiation of the crystals by the γ-quanta was performed by the ^{60}Co source with average energy about 1.25 MeV to the absorbed dose 10^2–10^7 Gy. Irradiation by the electrons with the average energy 1.25 MeV was carried out by electron transformer without the forced cooling to the absorption dose 10^3–5×10^7 Gy. To avoid the sample's heating the irradiation was done by the 0.5 s cycles with the next interval of 30 s. The temperature of the samples during the irradiation did not exceed 330 K.

4. Results and discussion

A simplified diagram of the SHG experiment is shown in Fig. 2. The diagram does not show the optical lenses, fibers and other additional elements used during the experiment. Pulsed Nd:YAG laser with 1064 nm wavelength and 5 ns duration time generated the higher harmonic in the RKTP crystals placed on the motorized precision rotation stage. Each sample was studied within the angle range from –35 °C to +35 °C with respect to the incident light. The filter at a wavelength of 532 nm with spectral range 10 nm cut-off the high energy fundamental laser beam thereby protected the sensitive CCD detector of the spectrometer. All experiment was controlled by LabVIEW program.

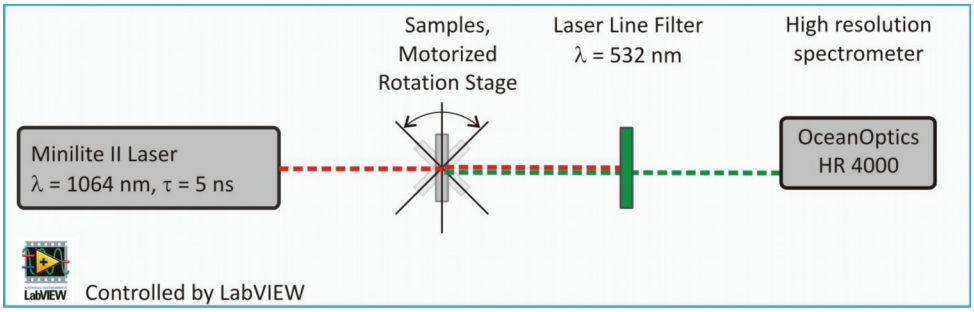

Fig. 2. Experimental set-up for the measurement of SHG.

The detection of the light was performed for the output polarization along the same axes. Varying the angle between the direction of the propagation and the direction of the optical axis we obtain the system of equations which allow us to obtain the values of the d_{33}.

As we can see from Fig. 3 maximum SHG signal for the $Rb_{99.8\%}K_{0.2\%}TP$ (crystal 1) is 5% for 14° of the angle of incidence. The $Rb_{99.0\%}K_{1.0\%}TP$ (crystal 2) shows better conversion efficiency. For the angle 12° the conversion efficiency is 8% with respect to the BiB_3O_6 (BiBO) single crystal. We have found that for non-irradiated samples with $x = 0.01$ the effective second-order susceptibilities determined from the powder--like micrometer samples were less than for the $x = 0.02$ and effective values of the second-order susceptibilities for 1064 nm were equal to 3.12 pm/V ($x = 0.002$) and

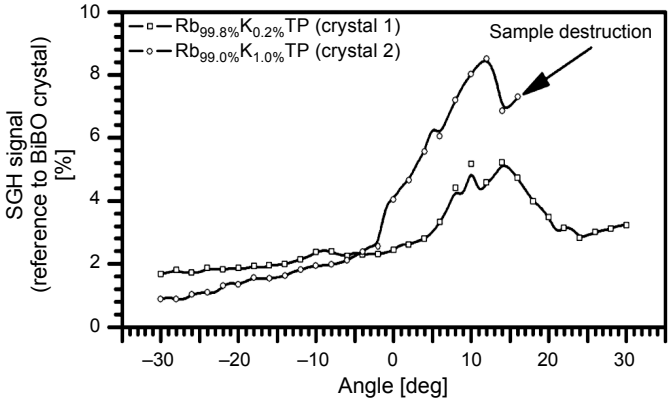

Fig. 3. $Rb_{99.8\%}K_{0.2\%}TP$ (crystal 1) and $Rb_{99.0\%}K_{1.0\%}TP$ (crystal 2).

2.56 pm/V ($x = 0.01$), respectively. After the gamma irradiation the corresponding values were equal to 2.45 pm/V and 2.78 pm/V. Moreover, for the samples with $x = 0.01$ one can observe damage occurring at the laser energy power about several J/cm^2. Such effect is absent for the pure KTP crystals and may be a consequence of substantial role of the intrinsic defects caused by insertion of the potassium ions in the positions of the rubidium ions.

To understand the origin of the effects it is necessary to take into account that during the cationic substitution of the stoichiometric KTP or RTP crystals there occur some differences in the cationic radii. The latter lead to changes of the effective cationic charges which are extremely sensitive to the external environment [17]. The external gamma irradiation causes an occurrence of defect centers, which may enhance local polarizabilities [18]. Figure 4 presents dependence of d_{33} on the irradiation time at 1.23 Gy produced by ^{60}Co source.

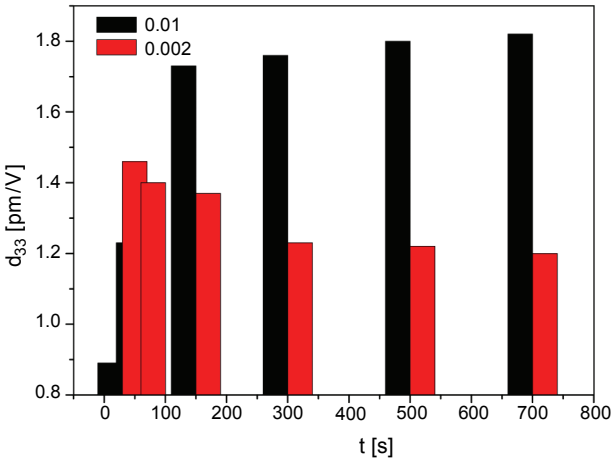

Fig. 4. Dependence of piezoelectric coefficients on the time of gamma irradiation treatment.

Following Fig. 4 one can see that the principal piezoelectric tensor component d_{33} for the RKTP crystals with $x = 0.01$ d_{33} increases with increasing gamma irradiation time and for $x = 0.002$ the corresponding SHG dependence shows an opposite behavior with respect to the SHG. So, generally, the sensitivity to the gamma irradiation has an inverse behavior with respect to the optical SHG. This fact may indicate that the defects stimulated by the gamma irradiation have different influence on occurrence of the local noncentrosymmetry causing the SHG and for the formation of the local electrostatic electric field responsible for the piezoelectric effects.

The data presented in Ref. [14] of the KTP show that there were not substantial changes of elastic constants. So the changes of the piezoelectric properties may be caused by the radiation stimulated charged defects.

Such process may be caused by different contribution of the charged defects to the polarizablity of the oxide ligand clusters [19] through the formation of the photoinduced piezooptical effects [20], optically induced electron–phonon interaction [21–23].

5. Conclusions

We have found that for non-irradiated samples of RKTP (with $x = 0.01$) the effective second-order susceptibilities determined from the powder-like micrometer-sized samples were less than for the $x = 0.02$ and the effective values of the second-order susceptibilities for the 1064 nm were equal to 3.12 pm/V ($x = 0.002$) and 2.56 pm/V ($x = 0.01$), respectively. After the γ-irradiation the corresponding values were equal to 2.45 pm/V and 2.78 pm/V. Moreover, for the RKTP samples with $x = 0.01$ one can observe the occurrence of the damage at the laser power energy about several J/cm^2. Such effect is absent for the pure KTP crystals and may be a consequence of intrinsic defects.

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