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KDP crystal doped with L-arginine amino acid: growth, structure perfection, optical and strength characteristics

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ABSTRACT

Potassium Dihydrogen Phosphate (KDP) crystal doped with L-arginine (L-arg) amino acid with 1.4 wt% concentration in the solution was grown onto a point seed by the method of temperature reduction. For the first time an attempt was made to grow large-size ($7 \times 6 \times 8$ cm^3) optically transparent crystals, which allowed to analyze the effect of L-arg additive on the physical properties of the different growth sectors ({100} and {101}) of KDP. The incorporation of L-arg into both growth sectors of the crystal was confirmed by the methods of optical and IR spectroscopy and found to be caused by the ability of the amino acid to form hydrogen bonds with the face {100} and electrostatically interact with the positively charged face {101} of KDP crystal. A slight variation in the unit cell parameters was reported, the elementary cell volume of KDP:L-arg crystal increased in comparison with the one of pure KDP by $2 \cdot 10^{-2}$ and $2.07 \cdot 10^{-2}$ Å^3 in the sectors {100} and {101}, respectively. It was found that the doping of L-arg enhanced the SHG efficiency of KDP and depended on the crystal growth sectors. The SHG efficiency of KDP:L-arg was by a factor 2.53 and 3.95 higher in comparison with those of pure KDP for {101} and {100} growth sector, respectively. The doping was found to lead to softening of both faces by ~3–10% and ~14–17% in the sectors {101} and {100}, respectively. Investigation of the influence of L-arg molecules on the bulk laser damage threshold of the crystals showed that the bulk laser damage threshold of the samples of KDP:L-arg crystal was higher than the one of the pure crystal in the sector {101} and lower in the sector {100}. The correlation between microhardness and laser damage threshold were discussed. The study is helpful for further searching, designing and simulation of hybrid NLO materials.

1. Introduction

Potassium Dihydrogen Phosphate (KDP, KH_2PO_4) single crystals attract much attention due to their wide applications in different fields of nonlinear optics, optoelectronics and photonics. These crystals have become popular owing to their transparency in the UV spectral region, high structure perfection, relatively high laser damage threshold and low cost of fabrication of optical elements, and are widely used as harmonic generators of high-powerful lasers and for electro-optical applications such as Q-switches [1]. KDP is a prototype of a family of crystals with bridging hydrogen bonds and its physical properties have been extensively studied [2].

However, one of the main functional restrictions for these crystals is relatively low value of quadratic susceptibility. With the aim of increasing the efficiency of the second harmonic generation for KDP crystals, numerous studies have been performed to find out possible methods for raising the efficiency of laser radiation conversion by modifying the structure of the well-known nonlinear optical single crystals (KDP, ADP) [3–9], or creating composite semi-organic nonlinear optical (NLO) media [10,11]. As shown by Xue et al. [12], hydrogen bonds (such as O–H··· and N–H···O) play a very important role in optical nonlinearities of inorganic crystals. For instance, L-arginine phosphate (LAP), a typical NLO semi-organic crystal, combines the advantages of both inorganic NLO crystals, e.g. high optical damage threshold, and of organic NLO crystals, such as considerable optical nonlinearity [13]. LAP belonging to KDP family crystals consists of alternating layers of the inorganic dihydrogen phosphate anionic groups, water molecules

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and the organic L-arginine (L-arg) molecules $[(H_2N)CNH(CH_2)_3CH(NH_3)COO]^+$, held together by plentiful hydrogen bonds [14]. The organic L-arginine molecule, the inorganic dihydrogen phosphate anionic group and the water molecules are all attributed to the NLO response of the crystal, but the major contribution is made by intrinsic optical nonlinearity of organic L-arg molecule and inorganic dihydrogen phosphate group [14].

In KDP family crystals hydrogen bonds essentially contribute to nonlinear optical phenomena such as quadratic electrooptical effect and generation of higher harmonics. Increase of the number of hydrogen bonds and optimization of their spatial location in the crystals make it possible to control the nonlinear optical characteristics of the crystals [2,12,15,16]. For raising the quadratic susceptibility and, consequently, the efficiency of the three-wave processes, there have been made many attempts to incorporate organic molecules such as acid molecules into KDP family crystals. Such molecules possess high polarizability due to the processes of internal charge transfer between the donor (COO^-) and acceptor (NH_2^+) groups [14]. As found in Refs. [17], the incorporation of a number of amino acids (L-arg, L-valin, L-proline) into the structure of KDP group crystals raises the efficiency of second harmonic generation (SHG). Boopathi et al. [18] report the effect of glycine amino acid on the optical and dielectric properties of KDP and show that the SHG conversion efficiency of glycine-doped KDP is 1.4 times higher than the one of pure KDP. As found by Rajesh et al. [19], the addition of 1 mol % of DL-malic acid improves the structure perfection of ADP and NLO properties of the host matrices. For KDP crystal doped with L-threonine (0.4 wt% of L-threonine in the solution) the efficiency of SHG exceeds that of the pure crystal by 1.24 times [20]. The effect of the doping with L-arg amino acid on the SHG efficiency of KDP is reported by Parikh K.D. et al. [3]. The efficiency of SHG in KDP:L-arg, grown with the addition of 0.3 wt% and 0.4 wt% of L-arg increases by a factor of 1.33 and 1.74, respectively, in comparison with that of pure KDP. When studying the effect of L-arg on the electrical properties of KDP single crystals, Meena et al. [21] show that the electrical parameters of the doped KDP diminish with the increase of L-arg concentration due to the reduction of L-defects mainly caused by creation of additional hydrogen bonds by the impurity which impedes the motion of protons. Govani et al. [22] give a detailed characterization of the mechanism of incorporation of L-arg amino acid into the structure of KDP crystal by infrared absorption and Raman spectroscopic measurements. The authors have shown that disturbance of the bonds N–H, C–H, and C–N of L-arg amino acid, provide successful incorporation of the additive into the crystals.

Despite a variety of experimental data which testify to the possibility of the obtaining of efficient nonlinear optical materials on the base of KDP group crystals doped with organic molecules [17–21], the processes of physico-chemical interaction of the impurities with KDP matrix is studied insufficiently. In particular, a number of papers report the presence of functional groups corresponding to amino acids in the IR spectra of KDP:L-arg crystals, that points to the entering of L-arg molecules into KDP crystal [3,22,23]. It should be noted that the process of incorporation of L-arg molecules into different growth sectors ({100} and {101}), as well as the form of the molecule in the crystal (amino acid or L-arginine phosphate) are still being discussed. As is known [1], the morphology of KDP crystals is formed by the tetragonal prisms ((100) and (010) faces) limited by two tetragonal pyramids with the faces (101) and (011). The chemical bonds formed in KDP crystal between the growth units are the ones between K^+ cations and $H_2PO_4^-$ anions, as well as the hydrogen bonds of the adjacent $H_2PO_4^-$ groups. The prismatic faces of KDP are terminated by alternating positive K^+ and negative $H_2PO_4^-$ ions [24]. Therefore, the face (100) is, on the whole, charged neutrally [25] and adsorbs the metal cations and the organic molecules (for instance, amino acids) which can form hydrogen bonds. The pyramidal growth sectors {101} are stacked in the mode of two layers of cations alternating with two layers of anions. Each layer consists completely of either cations or anions. After the negatively charged double layer ($H_2PO_4^-$) is formed, the potassium ions will join into the lattice site rapidly because of their small volume, low weight and the absence of preferred orientation as compared with $H_2PO_4^-$. So, the pyramidal face is always positively charged in the growth process. The adsorption of the anions on the positively charged (101) planes overcomes a lower energy barrier than that of the cations. Therefore, L-arg molecules, due to the presence of the amino and carboxyl groups in their structure, can form hydrogen bonds with the phosphate groups of KDP crystal faces ((100) and (010)), and the negatively charged group COO^- can participate in the Coulomb interactions with the faces (101) and (011).

In the present investigation, an attempt to grow large-size KDP crystals doped with L-arg additive was made with the aim of improving the NLO properties of KDP crystals meant for both academic and industrial use. It should be noted that the effect of amino acids including L-arg molecule on the structural, NLO and mechanical properties of different growth sectors of KDP crystals has not been experimentally proved so far. The grown crystals were characterized by means of several complementary methods such as optical spectroscopy, FTIR and Raman spectrometry, high-resolution X-ray diffraction (HRXRD), Vickers microhardness, measurements of the second harmonic generation efficiency and of laser induced damage threshold.

2. Experimental section

2.1. Crystal growth

The initial KH_2PO_4 salt was synthesized from the high-purity reagents H_3PO_4 and KOH, the concentration of the impurities (Fe, Al, Cr, Mg, Mn, etc.) in KH_2PO_4 salt did not exceed 10^{-5} wt%, L-arg amino acid (Aldrich) was used in the capacity of precursor. The mother liquors (pH 4.0 ± 0.1) prepared in accordance with the solubility curve at a saturation temperature of 50.9 °C were passed through fluoroplastic filters with 0.05 mm pore diameter and then overheated during 24 h at T = 80 °C. L-arg and orthophosphoric acid (85%, ultra-high purity) were mixed in equimolar proportions in aqueous solution to prepare crystalline L-arginine phosphate powder. The latter was filtered, washed and air dried in an oven at 50 °C. Pure KDP and KDP:L-arg crystals were grown from aqueous solutions onto 5 × 5 × 10 mm^3 point seed by the temperature reduction method in 6L crystallizer at the relative supersaturation σ~2% (Fig. 1). The temperature was lowered at rates of 0.3 °C/day and 0.4 °C/day for pure KDP and KDP:L-arg, correspondingly. To provide dynamic crystal growth conditions, the solution in the crystallizer was stirred at a rate of 70 rpm. The average crystal growth rate was 1.4 mm/day and 1.0 mm/day for pure KDP and KDP:L-arg, respectively, both crystals had well developed growth sectors {100} and {101}.

2.2. UV-vis-IR, Raman and FTIR spectrometry

The UV-vis-IR absorption spectra for all the samples were registered by a Lambda 35 PerkinElmer spectrophotometer (200–1100 nm). The Raman spectra were measured on a high-resolution micro-Raman spectrometer HR800 HORIBA Jobin Yvon operating at 633 nm with spectral and spatial resolution 0.25 cm^{-1} and ~5 μ, respectively. The scattered light was collected in a back-scattering configuration and recorded on a Peltier-cooled CCD camera. The crystals used for UV-vis-IR and Raman measurements