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Single Crystals of α–$LiIO_3$ Doped with L–arginine and L–nitroarginine

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Abstract. One of the essential crystals for technology is the hexagonal modification of lithium iodate (α–$LiIO_3$), which is endowed with nonlinear optical, pyroelectric, piezoelectric, acousto–optic properties. In recent years, a number of research groups studied physical and physiochemical properties of several single crystals (KDP, ADP, BTCA, ZTC) that were grown in the presence of various amino acids (L–alanine, L–glycine, L–arginine, L–lysine, etc.). In all these studies a positive effect on growth process and crystal quality is described for the amino acids being used as dopants in solutions. Based on the promising results of existing studies, in this work the effect of mixtures of the amino acids L–arginine and L–nitroarginine on α–$LiIO_3$ single crystals is presented. Studies of IR spectrum, UV–Vis transmittance, thermal properties and nonlinear optical activity have shown that the optical quality and physicochemical properties of the crystal were improved in the presence of amino acid dopands. Our data indicates that second harmonic generation activity of the crystals of α–$LiIO_3$ grown with L–arginine and L–nitroarginine dopants is 1.2 times higher than that of pure α–$LiIO_3$.

1. Introduction

Crystals with non–linear optical, pyroelectric, piezoelectric, acousto–optic properties are widely used in various technologies. Along with development of technologies, there is an increasing demand for crystals and subsequently higher requirements for their properties. In order to fulfill those requirements on one hand ways to improve the properties of currently used crystals are being investigated, and, on the other hand, novel crystals are being searched that exhibit the necessary properties.

Hexagonal modification of lithium iodate (α–$LiIO_3$), which is endowed with non–linear optical, pyroelectric, piezoelectric, acousto–optic properties [1] is an indispensable crystal employed in various technologies.

Our research group has an extensive expertise and achievements in both improvements of existing crystals as well as in the search of new ones [2–5].

It could seem that all the possibilities of improving the properties of single crystals grown in low temperature aqueous solutions are explored. However, in recent years the use of amino acids as dopands in the growth medium of single crystals, such as KDP, ADP, BTCA, ZTC, have led to discovery of the positive effect of L–alanine, L–glycine, L–arginine, L–lysine amino acids on the growth of aforementioned single crystals [6–8]. Based on the positive results of these studies, this work has moved forward to study the effect of mixtures of the amino acids L–arginine and L–nitroarginine on α–$LiIO_3$ single crystals. For comprehensive characterisation of the crystals grown in the presence of amino acid mixture, IR spectrum, UV–V is transmittance, thermal properties and nonlinear optical activity were studied.

2. Experimental part

As initial reagents we used L–arginine and L–nitroarginine (L–Arg, L–NNA 98%) purchased from “Sigma”, Iodic acid (HIO_3, ‘‘chem. pure’’ grade, white crystals) and Lithium hydroxide (LiOH, ‘‘chem. pure’’ grade) purchased from “Reachim”. After having them grown, the crystals

were characterized with various physico–chemical methods. Infrared (IR) spectra were recorded to identify the amino acid incorporated into the crystal and determine its amount [9]. The IR spectra were recorded on Nicolet 5700 spectrometer in the range 400–4000 cm^{-1} (resolution: $2cm^{-1}$, number of scans: 32). The absorptions of pure lithium iodate lie in a very narrow infrared range ($700–800cm^{-1}$), which allows to precisely determine the presence of even a very small amount of amino acid in the crystal. The transmission spectrum was obtained with in the wave length range of 190–1100nm with the help of PERKIN ELMER LAMBDA 800 UV visible spectrophotometer.

Second harmonic generation was examined by direct observation on the crystal using a pulsed YAG:Nd laser with passive Q–switching (duration of pulses 20ns, repetition rate 5Hz) [10].

3. Results and discussion

3.1. α–$LiIO_3$ crystal growth process (pure and doped with amino acids)

There are two methods of growing lithium iodate single crystals of hexagonal modification: I) isothermal evaporation of solution, II) convective flow of the solution [1, 11]. In this study, crystals were grown by evaporation method, which we have optimized over many years to obtain constant growth rate during the entire growth process – a very important aspect for obtaining homogenous and high–quality crystals.

Another important requirement for growth of single crystals from low–temperature aqueous solutions is the purity of the solution. Standard methods to achieve the required degree of purity of the mother solution for lithium iodate are not efficient. The traditional re–crystallization is not efficient because in the case of low amounts of unwanted additives (the coefficient of inclusion of certain dopants is nearly 1%). Rozin et al [12] found that in case of use of plate seeds during growth of lithium iodate in so–called phantom part the content of impurities is several orders higher than outside the phantom. Thus, a very efficient method for lithium iodate purification can be deducted.

Using a large number of plate seeds and by growing until the end of the phantom part, the unwanted components of the solution can be accumulated in the phantom part, thus resulting in a solution with very high degree of purity [13]. No more phantom is observed in a crystal grown from a solution purified with the mentioned method which is evidence of the purity of the solution.

We used small volume crystallizers to minimize solution loss during experiments.

Fig. 1. The crystallizers.

These small crystallizers (3 items) are installed in the same water bath to have the same temperature for all solutions (both pure and with amino acid doped). All crystallizer mixers, which are connected to the same engine, are rotated with the same speed as well. All created conditions

allow a constant growth speed during the whole crystal growth process. The equipment is shown in Fig. 1. The grown single crystals seeds were cut from the same single crystal and with the same size: 4 × 30 × 30 mm^3. The pH of mother solution was 2.0±0.2. The average growth rate of the crystals along the growth direction was V=0.5 mm/day. First, we grew 3 pure α–$LiIO_3$ crystals. After closing the phantoms, 5% L–arginine and 5% L–nitroarginine amino acids were added to the two solutions. The temperature was 33°C throughout the growth.

Fig. 2. Single crystals of a) pure α–$LiIO_3$, b) α–$LiIO_3$ doped L–arginine and c) α–$LiIO_3$ doped L–nitroarginine.

The dimensions of α–$LiIO_3$, α–$LiIO_3$ doped with L–nitroarignine and α–$LiIO_3$ doped with L–arginine crystals were 46 30×30mm^3, 49×30×30mm^3 and 44×30×30mm^3, respectively (Fig. 2).

3.2. Vibrational spectra

Vibrational spectra of the α–$LiIO_3$ doped with L–nitroarginine and L–arginine amino acids are shown in Fig. 3.

The absorption band of nujol is indicated by an asterisk in the spectrum.

The absorptions bands of pure lithium iodate lie in a very narrow infrared range (700–800 cm^{-1}), which will allow to precisely determine the presence of even a very small amount of amino acid in the crystal. Figure 3a shows an absorption line typical for the α–$LiIO_3$ group (780 cm^{-1} range). Figure 3b shows that α–$LiIO_3$, which is doped with L–nitroarginine, has specific absorption bands of the nitroarginine groups. 3380 cm^{-1} and 3157 cm^{-1} absorption bands in the range 3400–3100 cm^{-1} are typical of ν(N–H) stretching vibrations of the NH_3, NH_2, NH groups. The absorption bands 1666 cm^{-1}, 1640 cm^{-1}, 1573 cm^{-1}, 1514 cm^{-1} and 1410 cm^{-1}, which are in the range of 1670–1400 cm^{-1}, are typical of the δ(N–H) deformation vibrations of NH_3, NH_2, NH groups.

Fig. 3c shows that α–$LiIO_3$ doped with L–arginine has specific absorption bands of arginine groups. Absorption band 3396 cm^{-1} is characteristic of stretching vibrations ν (N–H) of NH_3, NH_2, NH groups. And the absorption bands 1633 cm^{-1},1569 cm^{-1} and 1526 cm^{-1} which are in the range of 1670–1500 cm^{-1}, are characteristic of the deformation vibrations δ (N–H) of NH_3, NH_2, NH groups. We assume that the absorption peaks in the 2750–1700 cm^{-1} range are due to hydrogen bonds and in the range 1160–1090 cm^{-1} is the absorption lines of rocking of CH_2 groups.

Based on the presence of these absorptions, the presence of L–nitroarginine and L–arginine in α–$LiIO_3$ crystal can be identified.

3.3. Optical examination

The transmittance spectrum of α–$LiIO_3$ doped with L–nitroarginine and α–$LiIO_3$ doped with L–arginine crystals in the UV–Vis range is shown in Fig. 4.

The transmittance of all crystals started from 290 nm, but in the range of 290–350 nm, pure crystals of α–$LiIO_3$ and α–$LiIO_3$ doped with L–nitroarginine have a lower transmittance than crystals doped with L–arginine.

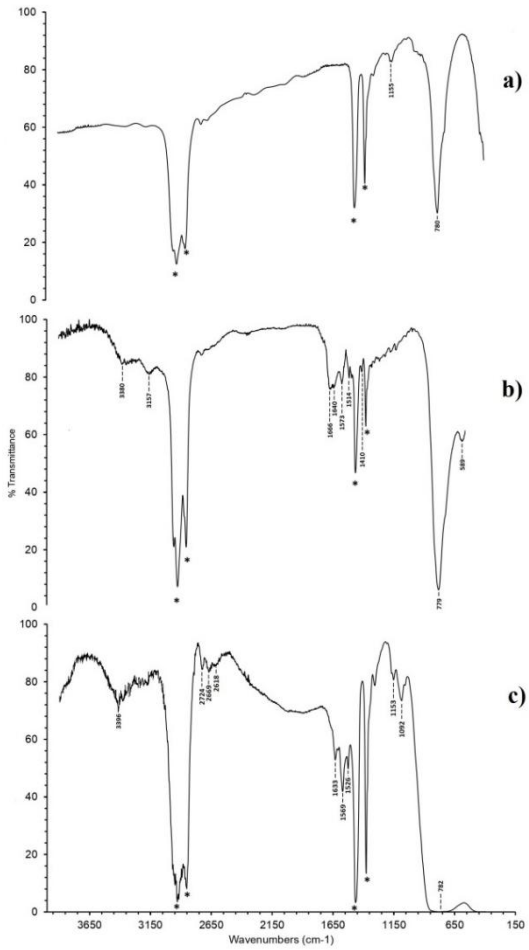

Fig. 3. Infrared spectra of a) pure α–$LiIO_3$, b) α–$LiIO_3$ doped with L–nitroarginine, c) α–$LiIO_3$ doped with L–arginine.

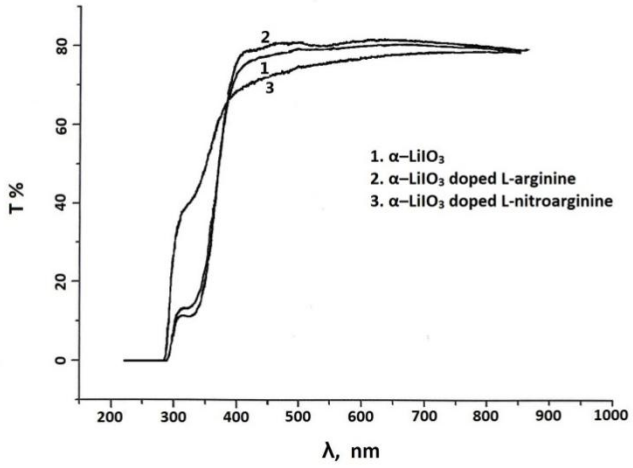

Fig. 4. UV–Vis. transmittance spectrum of grown crystals.

3.4. Nonlinear optical properties

Nonlinear optical activity was measured by the modified method of a powder [10] on installation using as a source of radiation pulse YAG:Nd the laser with passive modulation of good quality (duration of impulses of 20 ns, frequency of recurrence of 5Hz).

Second harmonic generation activity of the crystals of α–$LiIO_3$ grown with L–arginine and L–nitroarginine dopants is 1.2 times higher than that of pure α–$LiIO_3$ (Table 1).

Table 1. Nonlinear activity of α–$LiIO_3$, and their initial products.

Sample	$I^{2\omega}/I^{2\omega}_{KDP}$
α–$LiIO_3$	7.7
α–$LiIO_3$ doped with L–nitroarginine	9.1
α–$LiIO_3$ doped with L–arginine	8.9

4. Conclusions

The obtained experimental data showed that, according to preliminary data, for α–$LiIO_3$ crystals doped with L–arginine and L–nitroarginine is increased the growth rate, improved the quality of the crystals, optical permeability and second harmonic generation. Second harmonic generation activity of the crystals of α–$LiIO_3$ grown with L–arginine and L–nitroarginine dopants is 1.2 times higher than that of pure α–$LiIO_3$.

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