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Linear-nonlinear optical, dielectric and surface microscopic investigation of KH_2PO_4 crystal to uncover the decisive impact of dopant glycine

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Present investigation has been started to perform the comparative study of pure and glycine doped KH_2PO_4 (KDP) single crystals grown by most commercial slow solvent evaporation technique. The grown crystals were subjected to single crystal X-ray diffraction analysis to determine their structural parameters. The linear optical studies of pure and glycine doped KDP crystal have been undertaken within 200 nm to 1100 nm wavelength range by means of UV-Vis studies. The enhancement in second harmonic generation (SHG) efficiency of glycine doped KDP crystal has been determined using a standard Kurtz-Perry powder test. The dielectric measurements have been carried out to explore the impact of glycine dopant on dielectric constant and dielectric loss of KDP crystal. The surface growth habitat and etch pit density of glycine doped KDP crystal have been evaluated using the results of microscopic etching studies. In light of obtained results the suitability of glycine doped KDP crystal for device applications has been discussed.

Keywords: *crystal growth; dielectric studies; etching studies; nonlinear optical materials; optical studies*

1. Introduction

Since being identified as a promising nonlinear optical (NLO) material, potassium dihydrogen phosphate (KDP) crystal has drawn persistent attention of scientists throughout the globe and opened numerous possibilities in the field of nonlinear optics. The KDP crystal with exceptional qualities, including high growth rate, high nonlinear efficiency, large optical window and good ferroelectric and electro-optical properties, is a subject of interesting research extending its credibility for technological devices desirable for inertial confinement systems, optical data memory, laser fusion systems, frequency multiplication, optical switching, optoelectronics, optical modulators and laser engineering applications [1–5]. Looking at the strong technological impetus of KDP crystal over few decades, researchers have taken the challenge of upgrading its overall performance. In order to gain enhancement in characteristic features of KDP crystal, rigorous strategic attempts have been implemented such as (a) crystal growth using different techniques, (b) crystal growth by optimizing growth parameters (temperature, pH, solvent, recrystallization, etc.), (c) doping of additive [6–12]. Depending upon the priority of investigation, one can select either approach from

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the mentioned aforesaid ideas. However, in the literature, the doping technique is realized to be the most suitable idea when characteristic properties (structural, optical, mechanical, electrical and thermal) of particular crystal are to be customized. The keen inspection of the literature reveals that organic additives have prominent impact on distinct properties of KDP crystal amongst which additives from amino acid family play the most important role. Hitherto, discrete amino acids, such as L-tryptophan [13], L-arginine [14], L-aspartic acid [15], L-threonine [16], L-histidine [17], L-lysine [18], L-proline [19], L-alanine [20] and several more, have been used as a dopant and found to have conclusive impact on linear-nonlinear optical and dielectric properties of KDP crystal. In current investigation doping of glycine is proposed to achieve desirable gain in optical and electrical performance of KDP crystal. The present studies have been accomplished by means of crystal growth, X-ray diffraction, UV-Vis, Kurtz-Perry test, dielectric and etching characterization technique.

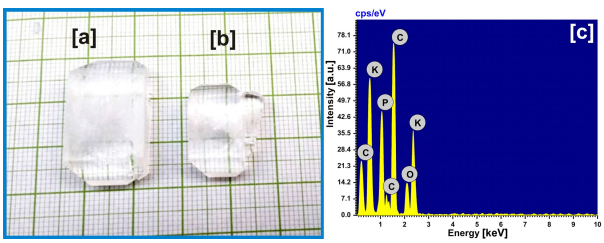

Fig. 1. (a) G-KDP crystal (b) KDP crystal, (c) EDS spectrum of G-KDP.

2. Experimental

Merck make AR grade potassium dihydrogen orthophosphate (KDP) salt was gradually poured into a beaker containing double distilled water until a homogeneous supersaturated solution of KDP was obtained. The 0.5 mol% of glycine dopant was precisely measured and added to the supersaturated solution of KDP. The glycine added KDP solution was allowed to mix for 6 h at constant speed. The solution was later filtered into a clean rinsed beaker using the No. 1 Whatman filter paper. This beaker containing the filtrate of glycine doped KDP was kept in a vibration free atmosphere to facilitate slow evaporation. Thorough precautions were taken by covering the beaker with a fine mesh to avoid inclusion of dust particles during crystal growth. The photograph of glycine doped KDP (G-KDP) and undoped KDP single crystal grown at 35 °C is shown in Fig. 1a and Fig. 1b, respectively.

3. Results and discussion

Energy dispersive spectroscopy is the most reliable technique to carry out the quantitative analysis of a grown crystal material. In present analysis, the EDS spectrum (Fig. 1c) of glycine doped KDP crystal has been recorded in the energy range of 0 keV to 10 keV using the Hitachi S4700 instrument. The detected elements, namely carbon, oxygen, potassium and phosphorous have been indexed at respective energy peaks in the spectrum. Thus, the presence of carbon evidences the successful doping of glycine in KDP crystal.

The structural analysis of the grown crystal has been performed at room temperature employing the single crystal XRD technique. The Enraf Nonius CAD4 single crystal X-ray diffractometer has been used to determine the structure, cell dimensions and space group of the grown crystals. The analysis of recorded XRD data shown in Table 1 reveals that the pure and glycine doped KDP crystal have the same structure and space group, however, the doping of glycine caused a slight change in unit cell dimensions of KDP crystal. This confirms that glycine has a significant impact on the lattice sites of the host KDP crystal.

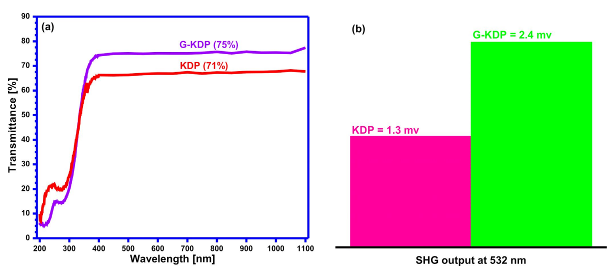

Fig. 2. (a) UV-Vis transmittance spectrum, (b) graphical representation of SHG output.

Table 1. Crystallographic data.

Crystal	Cell parameters [Å]	Volume [Å^3]	Crystal system	Space group
KDP	a = b = 7.451, c = 6.974	387.17	tetragonal	I42d
G-KDP	a = b = 7.456, c = 6.981	388.08	tetragonal	I42d

The light-matter interaction facilitates absorption of photon as a consequence of which electronic transitions occur in the material. This aforesaid fundamental process establishes the presence of optical transmittance in a given material, when scanned within a specific range of spectrum. The knowledge of optical transmittance helps to identify the suitability of a crystal for NLO device applications [21], therefore, in present investigation, the optical transmittance spectrum of pure and glycine doped KDP crystal (2 mm of thickness) shown in Fig. 2a has been recorded in the range of 200 nm to 1100 nm using a Shimadzu UV-1601 spectrophotometer. It is revealed that in visible region, the transmittance is 71 % for undoped KDP and 75 % for glycine doped KDP crystal. The transmittance of a crystal is controlled by the presence of optically active functional groups, orientation of molecules along the specified plane and the presence of defect centers. It is obvious that the presence of defect centers causes scattering/absorption of light in crystal medium which leads to the loss of optical signal [22–25]. The enhanced transmittance evident in glycine doped KDP crystal can be attributed to glycine doping which offers inherent low absorption characteristics of amino acid and suppresses the effect of structural/crystalline defects [26]. In the literature, glycine is found to be a potential dopant which favors significant rise in optical transmittance of bis-thiourea cadmium formate crystal, as evidenced in the literature [27]. The glycine doped KDP crystal with high optical transmittance and wide optical window might find advantage in designing components of UV-tunable lasers and transmission of harmonic signals of 1064 nm laser [28, 29].

The phenomenon of frequency doubling is most advantageous and appealing feature of NLO crystal. Therefore, the grown crystals have been subjected to a standard Kurtz-Perry test [30], using the Q-switched mode Nd:YAG laser operating at 1064 nm with the repetition rate of 10 Hz and pulse width of 8 ns. The powder samples of selected best crystals were prepared by grounding them into microgranules and further sieving in the quartz microcapillary tube of uniform bore. The samples were respectively irradiated by a Gaussian filtered beam of Nd:YAG laser. In addition, the output signal was channeled through the array of photomultiplier tubes and converted into electrical signal displayed on an oscilloscope. The response of each sample recorded at the input energy of 1.2 mJ is graphically presented in Fig. 2b. It reveals that the output response is 1.3 mV for KDP and 2.4 mV for glycine doped KDP crystal. The glycine doped KDP crystal is found to have 1.84 times higher SHG efficiency than KDP crystal. Besides, the major nonlinear optical response is facilitated by phosphate group of KDP [31]. The enhanced SHG efficiency originates due to several factors of glycine dopant, namely (a) noncentrosymmetric symmetry, (b) high dipole moment and (c) enhanced charge transfer over the donor-acceptor network [32]. In the literature, it is reported that doping of glycine has constructive impact on SHG efficiency of bis-thiourea cadmium formate [27] and bis-thiourea zinc acetate [33] crystals. The observed enhancement in SHG efficiency of KDP crystal due to glycine dopant is superior to that facilitated by other amino acids namely L-aspartic acid (1.06) [15], L-histidine (0.93) [18], L-arginine (1.77) and L-alanine (1.67) [20]. This pronounces the vital importance of glycine as a dopant.

The dielectric constant and dielectric loss of pure and glycine doped KDP crystal (1.8 mm thick) has been measured within the temperature range of 30 °C to 90 °C using a HIOKI-3532 LCR meter keeping the constant frequency of 100 kHz. The dielectric parameters of the crystal can be tuned by external factors such as frequency

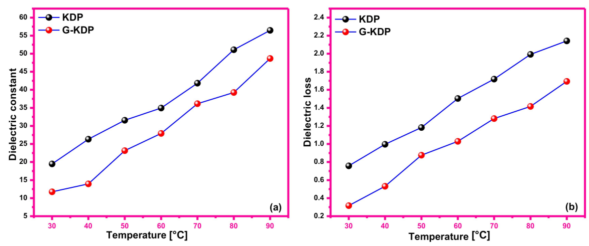

Fig. 3. Response of (a) dielectric constant, (b) dielectric loss.

and temperature [34, 35]. In particular, the response or relaxation of polarization domains to an applied frequency and temperature leads to the physical origin of unique behavior of dielectric constant. The electronic, ionic, dipolar and space charge activity is an integral part of polarization domains [36]. The variation of dielectric constant of pure and glycine doped KDP crystal is shown in Fig. 3a. It reveals that the dielectric constant of pure and glycine doped KDP crystal increases with each step of rising temperature. The increase in dielectric constant is facilitated by the dominance of space charge polarization at lower frequency and higher temperature [36, 37]. It is noticeable that doping of glycine results in decrease of dielectric constant of KDP crystal, which causes that glycine doped KDP crystal offers less power consumption, reduced Rc delay and minimum contact with adjacent connections [38] which is the most desirable parameter for fabricating THz wave generators, field detectors, photonic and electro-optic modulator devices [39]. According to Miller [40], material exhibiting lower dielectric constant offers high SHG efficiency coefficient which is in agreement with the present study. The dielectric loss determines the loss of electromagnetic signal during propagation through a crystal which is dependent on the factors, such as phonon interactions, micro-macro cracks, porosity, grain boundaries and randomly grown crystal faces [41, 42]. It is observed that the dielectric loss (Fig. 3b) has the same profile as the one of dielectric constants. The lower dielectric loss confirms that the glycine doped KDP crystal possesses lower concentration of electrically active defects [43]. The observation leads to the conclusion that glycine doped KDP crystal with lower dielectric loss satisfies the prerequisite for aforesaid applications which makes it a potential candidate for designing technological devices.

The chemical etching is an advantageous technique that aids to uncover microstructural imperfections, surface morphology, crystal defects, presence of dislocations and lattice inhomogeneity occurring along the studied crystal plane [44–47]. In particular, the defects associated with crystal surface can be categorized in dimension as (a) 0-D point defects: impurities, vacancies, interstitials, (b) 1-D line defects: dislocations, (c) 2-D planar defects: interfacial defects such as grain boundaries and phase boundaries, (d) 3-D bulk defects: voids, cracks, pores [48].

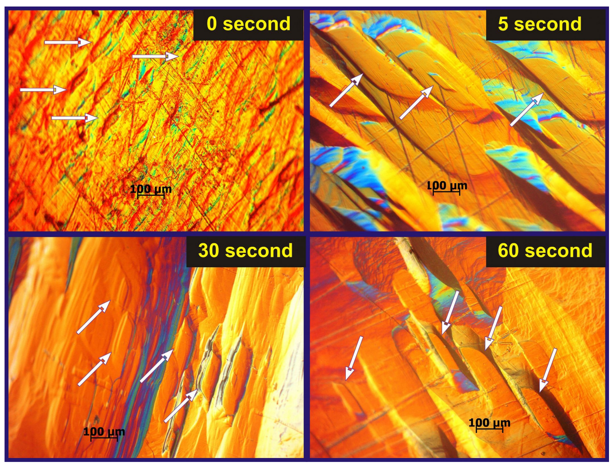

Fig. 4. Etch patterns of G-KDP crystal.

In the current study, the etch patterns of selected glycine doped KDP crystal surfaces have been captured in reflection mode using a Carl Zeiss optical microscope which was optimized to the magnification of ×50. Microimages captured in regular interval of time are shown in Fig. 4. They reveal that the as-grown crystal surface possesses irregular striations and randomly oriented micropits which are indicated by arrows. As dissolution of crystal in etchant reveals the occurrence of etch pattern at dislocation sites [49], the analysis of the microimage captured after 5 s of etching uncovers the presence of several fading striations with unique rectangular etch pattern which are slightly elongated at the edges. Further etching for 30 s and 60 s results in elongation of the etch pits, however, their shape remains the same. Similar phenomenon of etch pits elongation has been observed in NLO crystals reported in the literature [50–53]. It is noticeable that etch pits become more visible with an increase in etching duration which might have been facilitated due to segregation of impurities and dislocations. The occurrence of similar etch patterns throughout the surface confirms the uniform growth mechanism of the crystal along the studied surface. The etch pit density (EPD) of glycine doped KDP crystal is, thus, found to be 2.8×10^3 cm^{-2}.

4. Conclusions

Good quality glycine doped KDP bulk single crystal of dimensions 28 mm × 18 mm × 6 mm for optical device applications has been grown from aqueous solution by slow solvent evaporation. The incorporation of glycine in KDP crystal matrix has been established by EDS analysis. The single crystal XRD analysis confirmed a slight change in the cell dimensions of KDP crystal due to addition of glycine dopant, keeping the tetragonal structure and I42d space group of the host crystal unaltered. The optical transparency of glycine doped KDP crystal was found to be 75 % within entire UV-Vis range which is 4 % higher than that of parent KDP crystal. In Kurtz-Perry test, the glycine doped KDP crystal exhibited frequency doubling phenomenon with SHG efficiency 1.84 times higher than that of KDP crystal. Dielectric measurement studies revealed that the dielectric constant and dielectric loss of KDP crystal were successfully tuned to lower magnitude by the glycine dopant. The microscopic etching studies revealed the occurrence of unique rectangular etch patterns throughout the crystal surface confirming the uniform growth mechanism. The EPD of glycine doped KDP crystal was found to be 2.8×10^3 cm^{-2}. The glycine doped KDP crystal with outstanding optical, dielectric and surface qualities is suggested as a potential candidate for frequency convertors as well as optoelectronic and photonic device applications.

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