Effect of L-Threonine Doping on Structural, Optical, Mechanical, Surface and Dielectric Properties of KDP Single Crystal

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Abstract

KDP single crystals were grown from aqueous solution with different doping concentrations (1, 5 and 10 mol%) of L-Threonine (LT) by slow evaporation solution technique (SEST). The growth rate was found to enhance due to doping. The structural studies were carried out by powder XRD and FT-Raman spectroscopy and these studies reveal that there was no change in structure due to doping except variation in the Raman intensity. The photoluminescence (PL) study reveals that the PL intensity is varying with doping concentration. The etching study shows that the density of dislocations in the crystals is decreasing with doping concentration up to 5 mol% and increases above this concentration. The influence of the doping on mechanical and dielectric properties has been studied. From all these studies it was observed that the doping of LT improves growth rate, crystalline perfection, optical, mechanical and dielectric properties of KDP single crystals.

Keywords: Crystal growth; FT-Raman spectroscopy; Optical properties; Microhardness; Fracture toughness; dielectric properties.

Introduction

In the recent past immense importance has been given to nonlinear optical materials due to their wide applications in modern technology. Potassium dihydrogen phosphate (KDP) is a unique example of hydrogen bonded materials and exhibit piezoelectric, ferroelectric, electro-optic and nonlinear optical properties. KDP crystals have
attracted many researchers due to their simple structure and fascinating properties associated with a hydrogen bond system involving a large isotope effect, wide transparency window, high optical damage threshold and relatively low production cost [1]. KDP can be used in large aperture laser systems for fusion experiments [2,3]. Organic or inorganic additives or dopants were found to change or enhance the properties considerably like optical, mechanical, thermal and dielectric properties of single crystals [4-8]. KDP single crystals with enhanced properties will be useful for variety of device fabrications [9-13]. The mechanism of incorporation of organic molecules into the crystal lattice of KDP is discussed [14,15], where an essential role of local stereochemical affinity between the impurities and the matrix is considered. To the best of our knowledge there is no report on the effect of L-threonine (LT) organic amino acid doping on growth rate, structural, optical, mechanical, dislocations and dielectric properties of KDP single crystals.

In view of this, in the present investigation, KDP single crystals were grown with different molar concentration of LT doping. The structural, optical, mechanical, dislocation and dielectric studies were carried out by powder XRD, FT-Raman, photoluminescence spectroscopy, Vickers micro-hardness tester, chemical etching and impedance analyzer. The results are discussed in detail.

**Experimental procedure**

*Crystal growth*

Pure and LT doped KDP single crystals have been grown in the aqueous solution by slow evaporation solution technique (SEST) at room temperature in a constant temperature bath (CTB) to avoid the fluctuation in the temperature. LT was doped in the saturated solutions of KDP (1, 5 and 10 mol%) and these solutions were continuously stirred for 24h to get the homogeneous mixing of the dopant. The prepared solutions were filtered in beakers covered with perforated lids and kept in the CTB at room temperature for slow evaporation. After a span of a week, good quality visually transparent single crystals with enhanced size as the doping concentration increased were harvested (Fig.1) showing an enhanced growth rate due to LT-doping.

![Figure 1: Photograph of as-grown crystals of KDP (a) pure, (b) 1 mol%, (c) 5 mol%](image-url)
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and 10 mol% LT doped.

Analysis techniques

Good quality single crystals of pure and LT doped KDP were crushed to prepare fine powders. The prepared powders were filtered using a standard sieve with 20 microns (MICs) aperture openings to get homogeneous particle size. These powdered specimens were loaded in to the circular sample holder and subjected to PW3710 based Philips analytical powder X-ray diffractometer to record the XRD patterns having CuKα radiation at the scan rate of 0.01˚/s over the angular range of 5-70˚ at room temperature. For FT-Raman studies, Perkin Elmer GX 2000 FT-RAMAN spectrometer in the range of 100–3500 cm⁻¹ with the resolution of 1 cm⁻¹ has been used to carry out the vibrational studies of pure and LT doped KDP crystals. PL study of the pure and doped single crystals using (200) planes has been carried out in the wavelength range of 500-800 nm using in house developed PL spectrophotometer with the Argon ion laser excitation source at 480 nm at room temperature. Chemical etching technique has been employed to study the dislocations in these crystals by using Magnus MLX microscope fitted with Motic (1000) camera. The microhardness study was carried out on (101) faces of the pure and LT doped KDP single crystals using Vickers microhardness tester fitted with diamond indenter. A PSM 1735 impedance analyzer was used to carry out the dielectric measurements. Pure and doped single crystal specimens were prepared in the rectangular shape (size: 6×4×2 mm³) and conducting electrode plates were made on the two opposite parallel surfaces using good quality silver paste. These have been dried in the oven at 60 °C to remove the moisture. The dielectric constant, dielectric loss and ac conductivity were measured over a wide range of frequency (100Hz-1MHz) at ambient temperature.

Results and discussion

Powder X-ray diffraction and FT-Raman analysis

The PXRD patterns of pure and LT doped KDP crystals were recorded (Fig. not shown). The 2-theta values were used to confirm the crystal system and calculated the lattice parameters by ‘POWDERX’ refinement. The lattice parameters for all the specimens remain almost same and contribute to the same cell volume as presented in Table 1, which clearly depict that doping does not affect the structure of the crystal. The calculated lattice parameters as given in Table 1 for all the specimens are in good agreement with those of earlier reported values [16].

![Table 1: Lattice parameters of as grown and LT doped KDP single crystals.](image)
The FT-Raman spectra of pure and doped specimens were recorded for (101) planes at room temperature in the wavenumber range of 100 to 3500 cm\(^{-1}\) as shown in Fig. 2 (a). The FT-Raman spectra of pure, 1.0, 5.0 and 10.0 mol% LT doped KDP single crystal specimens contain all the internal modes of vibrations [17, 18]. The close view of the main peak at 914 cm\(^{-1}\) has been shown in Fig. 2 (b). From figure 2 (b), it is clear that the Raman intensity of the peaks is decreased for 1, 5 mol% and then increased for 10 mol% of LT doping concentration in KDP crystals. The intensity variation due to doping may be due to the defects present in the crystals. The vibrational modes present in the doped crystals are same as in the pure crystal. The small scattered intensity around 210 cm\(^{-1}\) belongs to the lattice vibration modes of the crystal. All the above modes of vibrations are corresponding to the tetragonal phase of KDP crystal, and the similarity of all spectra confirms that the crystalline phase of crystal does not vary with the doping concentration of LT.

![Figure 2 (a): FT-Raman spectra of pure and doped KDP crystals and (b) close view of the main peak.](image)

**Photoluminescence (PL) analysis**

The observed PL spectra of the single crystal specimens are shown in Fig. 3. For pure and LT doped KDP crystals, a very broad emission band is observed around at \(\lambda_{\text{max}}=590\) nm with very low luminous intensity [12]. The blue shift of \(\Delta\lambda=30\) nm for 1 and 10 mol% doped crystals has been observed with \(\lambda_{\text{max}}=560\) nm compared to that of pure KDP and 5 mol% LT doped KDP specimens. For 5 mol% doped crystal, the intensity of emission band is of maximum intensity but at the same position (\(\lambda_{\text{max}}=590\) nm) of pure crystal. At the lower concentration (1 mol%), very few dopant molecules get incorporated in the crystal matrix to act as the defect luminescence centers. Similarly, at highest concentration (10 mol%), the crystalline matrix cannot accommodate large number of dopant molecules and these are likely to get segregate along the grain boundaries due to the stresses [19]. Therefore, even at such high concentrations only a very few isolated dopant molecules may be accommodated by the lattice to act as the luminescence centers [20]. For 5 mol% doping good number of the dopant molecules might have entered inside the lattice matrix at the interstitial
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position without the formation of clusters and act as the color centers.

![Photoluminescence spectra of pure and LT doped KDP single crystals.](image)

**Figure 3:** Photoluminescence spectra of pure and LT doped KDP single crystals.

**Etching studies**

Chemical etching technique has been employed to study dislocations in these crystals using Magnus MLX microscope fitted with Motic (1000) camera. Out of the several etchants tried like acetic acid and formic acid, different ratios of acetic and formic acids, the best etching action was observed with water revealing rectangular etch pits suggesting that these faces possess minimum two-fold rotational symmetry as shown in Fig. 4. Pure and LT doped KDP single crystals were etched with water for etching time of 2 sec. The longer side of etch pit is parallel to longer edge of the crystals. The etch pits micrograph shows that the pure crystal is having more dislocation density in comparison with LT doped crystals and as the doping concentration increases, density of dislocations decreases up to 5 mol% and later increased. The average dislocation density for pure, 1, 5 and 10 mol% KDP crystals are respectively $5 \times 10^4$/cm$^2$, $3.6 \times 10^3$/cm$^2$, $3.1 \times 10^2$/cm$^2$ and $4.5 \times 10^2$/cm$^2$. The above values indicate that the doped crystals up to 5 mol% concentration have better crystalline perfection than pure KDP crystals.
**Figure 4:** Etching pattern of pure and LT doped KDP single crystals.

**Vickers micro-hardness analysis**
Mechanical strength of the material plays a key role in device fabrication. It is a measure of the resistance offered by the lattice for permanent deformation. Hardness is an important strength parameter of a crystal, and these tests are non-destructive in nature. Vickers microindentation hardness studies were carried out using Leitz-Wetzlar hardness tester equipped with a diamond square indenter. Loads ranging from 10 to 100 g were used for these studies with a constant indentation time of 15 sec for all these crystals. The distance between any two consecutive indentations was kept more than five times the diagonal length of the indentation mark in order to avoid the surface effects. For the hardness studies, (101) faces of the crystals were ground with SiC paper down to 600 grit and then polished with methanol solution to remove the surface damages. Indentations were made with Vickers Microhardness tester. At least five indentations were made on (101) face of pure and LT doped KDP crystals at each load. The average diagonal length of the indentation impression at each load was used for measuring microhardness value \((H_v)\). The mechanical contact between the indenter and the crystal surface produces radial cracks. So, fracture toughness value \((K_c)\) which is another mechanical parameter was determined by measuring the crack lengths of radial cracks. The hardness of the crystals is calculated using the relation:

\[
H_v = 1.854 \frac{P}{d^2} \text{ kg/mm}^2
\]  

(1)

Where \(H\) is the Vickers hardness number, \(P\) is the indentation load in kg and \(d\) is the diagonal length of the impression in mm. The microhardness value was taken as the average of the several impressions made.

The hardness estimated in these samples are showing normal trend that as load increases, hardness decreases and reaches to load independent region [Fig. 5 (a)]. Such load dependence hardness is observed in a variety of materials like metals [21], alkali halides [22, 23].

The relationship between load and size of the indentation is given by Meyer’s law,

\[
P = K_1d^n
\]  

(2)

where \(P\) is the load applied, \(d\) is the diagonal length of impression, \(K_1\) is a constant and \(n\) is the Meyer’s index (or work-hardening co-efficient). From the slope of \(\ln P\) vs \(\ln d\) plots shown in Fig. 5 (b), \(n\) value is estimated and given in Table 2. Onitsch [24] and Hanneman [25] had shown that the value of \(n\) comes out to be 1-1.6 for hard materials and more than 1.6 for soft ones. Thus the present crystals under study belong to hard material category. According to Hays–Kendall approach [26] load dependence of hardness is given by,

\[
P = W + A_1d^2
\]  

(3)

where \(W\) is the minimum load to initiate plastic deformation and \(A_1\) is a load independent constant. These two values have been estimated from the plots drawn between \(P\) vs \(d^2\) shown in Fig. 5 (c), where \(W\) is the intercept along the load axis and \(A_1\) is the slope. The corrected hardness \(H_o\) for these crystals has been estimated using the relation:

\[
H_o = 1854 \times A_1
\]  

(4)
The \(n\), \(W\) and \(H_o\) values for pure and LT doped KDP single crystals are given in Table 2.

\[ \text{Figure 5 (a): Variation of Vickers hardness } H_v \text{ with load } P \text{ and (b) Plots of } \ln P \text{ versus } \ln d \text{ (c) } P \text{ versus } d^2 \text{ plots for pure LT doped KDP crystals.} \]

**Fracture toughness, Brittle index and yield strength**

Resistance to fracture indicates toughness of a material. The \(K_c\) determines how much fracture stress is applied under uniform loading. It is an important parameter for the selection of materials for application where the load exceeds the limit or yield point [27]. The cracks developed on a crystal determine the fracture toughness \(K_c\). Crack lengths \(l\) were measured from the centers of the indentation to the tip of the crack. In the present studies well defined cracks at the corners of the indentation appear for \(P \geq 40\) g. The crack length bears a linear relationship with applied load [Fig. 6 (a)]. Then under equilibrium conditions [28] the measurement of fracture toughness is given by

\[ \frac{P l^{3/2}}{l} = \beta_o K_c; \quad l \geq d/2 \]  

where \(K_c\) is in \((g/\mu m)^{3/2}\), \(l\) in microns and \(\beta_o\) is the indenter constant, taken as 7 for Vickers diamond indenter [29]. The variation of estimated \(K_c\) value using above equation at each load is shown in Fig. 6 (b). Strong dependence of \(K_c\) on surface crack length suggests that it is an indication of a residual surface stress. Variation of crack length and fracture toughness on load can be attributed to the depth of penetration of the indenter into the surface [30]. Britteness is another important property of a crystal which gives us an idea about the fracture induced in a material. It is expressed in terms of brittleness index \(B_i(\mu m)^{-1/2}\) [31] and it is computed using the relation:
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\[ B_i = \frac{H}{K_c} \]  \hspace{1cm} (6)

The variation of brittleness index with load for pure and LT doped KDP crystal is shown in Fig. 6 (c). From the hardness values, the yield strength can be calculated [25] using the relation:

\[ \sigma_y = \frac{H}{3} \text{ (only when } n < 2) \]  \hspace{1cm} (7)

The \( K_c \), \( B_i \) and \( \sigma_y \) values for pure and LT doped KDP single crystals at load independent hardness region \( (P = 100 \text{ g}) \) are given in Table 2.

![Figure 6](image_url)

**Figure 6 (a):** Variation of crack length \( l \) with load \( P \), (b) Variation of fracture toughness \( K_c \) with load and (c) Variation of Brittle index number \( B_i \) with load.

**Dielectric analysis**

Dielectric study results have been shown in Fig. 7, the dielectric constant \( (\varepsilon_r) \) in Fig. 7 (a) is higher at lower frequencies and decreases with increase in the frequency. At lower frequencies all the four types of polarization (space charge, dipolar, ionic and electronic) contribute to the higher values of dielectric constant \( (\varepsilon_r) \) [32]. As the frequency increases only ionic and electronic polarization contribute to \( \varepsilon_r \). The value of \( \varepsilon_r \) increase with doping concentration at lower frequencies and it attains maximum value for 10 mol\% doped KDP crystals. Similar behavior has been observed for dielectric loss (\( \tan \delta \)) [Fig.7 (b)]. The ac conductivity \( (\sigma_{ac}) \) has been calculated [Fig. 7 (c)] using the formula \( \sigma_{ac} = 2 \pi f \varepsilon_0 \varepsilon_r \tan \delta \), where \( f \), \( \varepsilon_0 \), \( \varepsilon_r \) and \( \tan \delta \) are frequency of the applied ac signal, vacuum permeability, relative permeability and dielectric loss of the material respectively. For pure, low and medium concentration doped crystals, the \( \sigma_{ac} \)
values are very low up to 10 kHz and above this frequency it increases very fast, following the frequency power law [33,34]. For 10 mol% LT doped crystal specimen $\sigma_{ac}$ values are higher at low frequencies then decrease in the mid frequency region and at higher frequencies follow the similar behavior that of other specimens. Such a behavior of $\varepsilon_r$ and tan $\delta$ for pure, low and medium concentration doped KDP crystals confirms that pure and lower concentration doped crystals have low density of defects whereas at higher concentrations (> 5 mol%), defects are more.

![Dielectric Constant, Dielectric Loss, and AC Conductivity Plots](image)

**Figure 7:** Dielectric studies plots (a) dielectric constant, (b) dielectric loss, and (c) AC conductivity for pure and doped KDP single crystals.

**Conclusions**

The LT doped single crystals of KDP were grown successfully with enhanced growth rate. The powder XRD confirms the crystal structure. FT-Raman study reveals that all the vibration modes are unaffected except a slight variation in the intensity of Raman peaks with the doping of LT. From the PL spectra, the blue shift of $\Delta\lambda=30$ nm for 1 and 10 mol% doped crystals has been observed with $\lambda_{max}= 560$ nm compared to that of pure KDP and 5mol% LT doped KDP specimens. For 5 mol% doped crystal the intensity of emission band is maximum but at the same position ($\lambda_{max}= 590$ nm) of pure crystal. The etching study reveals that the dislocations in the doped crystals are decreased for 1 and 5 mol% and then increased for 10 mol% but still less than pure KDP. The mechanical properties on (101) face of pure and LT doped KDP crystals were analyzed using microindentation technique. The hardness depends on load; as load increases, hardness decreases and reaches to load independent region for all molar concentrations and the behavior is explained on the basis of dislocation motion. The Meyer’s index number $n$ decreased with doping concentration and shows that hardness of the material increased due to LT-doping. The dielectric constant and loss
values are consistent for doped crystals with those of pure crystal at higher frequencies, whereas at lower frequencies these values increase with doping concentration. LT-doping in KDP leads to enhance growth rate, crystalline perfection, photoluminescence, hardness and dielectric behavior and hence it is useful for the fabrication of KDP based electro-optic devices.

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