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GROWTH AND CHARACTERIZATION OF METAL DOPED KDP CRYSTALS FOR OPTOELECTRONIC APPLICATIONS

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ABSTRACT

Metal (Li^{2+}) doped potassium dihydrogen phosphate (KDP, KH_2PO_4) crystals are grown slow evaporation method by solution growth technique. The changes in the structural, optical, mechanical and thermal properties were observed. The prominent peak in the Powder XRD pattern confirms the crystalline nature of the sample. Optical studies reveal that the crystal is transparent in the entire visible light region. Thermal stability was confirmed by TG/DTA analysis. The mechanical properties were evaluated from the Vicker's micro hardness test. Metal doping improved the NLO properties. The micro structural morphology and the elemental composition of the doped specimen was obtained from SEM and EDX analysis. The detailed results on the spectral parameters, habit modifications and constant values will be presented.

KEYWORDS

Single Crystal XRD, FTIR, UV, Hardness, SHG and NLO.

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INTRODUCTION

Potassium dihydrogen orthophosphate (KDP) has gained considerable interest because of its wide and high frequency conversion and high damage threshold against high power laser. KDP has been extensively studied formany years due to its important applications such as second harmonic generation, Q-switch and quantum electronics[1,2]. KDP and ammonium dihydrogen phosphate (ADP) are nonlinear optical materials and have been used as optical modulation devices and frequency converters. The National Ignition Facility (NIF),

being built at Lawrence Livermore National Laboratory (LLNL), requires large single crystal plates of KDP (KH_2PO_4) and DKDP (KD_2PO_4) for Pockels cells and frequency converters as a part of its design[3]. Particularly, optical crystals with lower impurity and higher damage threshold are required for inertial confinement fusion. The KDP is a transparent dielectric material best known for its nonlinear optical and electro-optical properties. Because of its nonlinear optical properties, it has been incorporated into various laser systems for harmonic generation and optoelectrical switching[4]. The very high-energy Nd:glass lasers used for inertial confinement fusion research need large plates of nonlinear crystals for electro-optic switches and frequency converters[5]. KDP crystal draws persistent attention of scientists due to its excellent quality and possibility of growing large-size single crystals[6-8]. KDP finds widespread use as frequency doublers in laser applications and has been studied at great detail. KDP, ADP and DKDP are the only nonlinear crystals currently used for these applications due to their exclusive properties. These properties include transparency in a wide region of the optical spectrum, resistance to damage by laser radiation, and relatively high nonlinear efficiency, in combination with reproducible growth to large size and easy finishing. In all the methods of growth, planar habit faces contain separate regions common to each facet having their own sharply defined growth direction known as growth sectors. The boundary between these growth sectors is more strained than the extended growth sectors due to mismatch of lattices on either side of the boundary as a result of preferential incorporation of impurities into the lateral section[9].

One of the major growth inhibitors in the KDP system is the transition metal ions like Fe and Cr which are inherently present. For the great majority of elements, K has a tendency to decrease with increasing impurity concentration in the solution. The decrease is particularly strong in the second group of cations, increasing the initial Co^{2+}, Mn^{2+}, and Ni^{2+} concentrations by one to two orders of magnitude reduces K by one to three orders of magnitude. However, this effect, typical of M^{2+}cations, is much weaker in the case of trivalent cations, which occupy the same interstitial position in the structure of KDP[10]. The effect of cerium on the growth and the crystalline quality of KDP crystals was investigated and reported[11]. The impact of Titanium dioxide (anatase) nano crystals on the structural and optical properties of KDP crystals was studied by Igor Pritula *et al*,[12]. Trivalent impurity Chromium (Cr III) increases the mean growth rate along the (001) direction[13]. The same observations were done for Fe III by Owezarek and Sangwal[14]. Effect of KCl doping in KDP was also reported[15]. Ambhore *et al*. investigated and reported the effect of doping NaCl with KDP[16].

To analyze the influence of metal ion based dopants on the nonlinear optical property of KDP crystals, efforts were made to dope KDP with metal. The effects of impurity atoms on the quality and performance of the material are analyzed. In the present work adding Lithium Chloride (Li^{2+}) into the crystal lattice of potassium dihydrogen phosphate (KDP) and its characterizations are reported. The structural, chemical, optical, mechanical and nonlinear optical properties of the doped crystals were studied with the characterization studies such as powder XRD, FT-IR, Thermal and SHG measurements, respectively. The results for metal doped KDP are compared with the results of the pure KDP crystals.

Crystal growth

Commercially available AR grade potassium dihydrogen phosphate (KDP) salt of 99.8% purity was purchased from Merck Company. Calculated amount of KDP salt was dissolved in deionized water and saturated solution of KDP was prepared. To the saturated KDP solution 1mol% of Lithium Chloride were added. The solution was continuously agitated for 5hours at room temperature for the homogenization of the solute particles. Then the clear solutions are filtered in a clean beaker and kept in a dust and vibration free atmosphere. Colourless transparent crystals were obtained after period of 25 (undoped), 30 (Li^{2+}) days. The photographs of the grown undoped and metal doped KDP crystals are shown in the Figure No.1a and 1b.

Single Crystal X-Ray, Powder X-Ray diffraction analysis

Single crystal X-ray diffraction analysis reveals the structural characters and lattice parameters of the undoped and Li^{2+} doped KDP crystals. The single crystal X-ray diffraction pattern of the undoped and Li^{2+} doped KDP single crystals was recorded using ENRAF NONIUS CAD4 automatic X-ray diffract to meter and the structure was solved using SHELXL program. The indexed X-ray powder diffraction pattern of 1 mol % Li^{2+} doped KDP and undoped KDP crystals is shown in Figure No.2a and 2b.

The analysis revealed that both the undoped and Li^{2+} doped KDP single crystals crystallize in tetragonal system with the space group of I42d. The estimated lattice parameters of undoped KDP are a=b= 7.43 Å, c=6.95 Å and α=β=γ= 90°. The volume of the unit cell was found to be 383 $Å^3$. The lattice parameters for Li^{2+} doped KDP are a=b=7.49 Å c= 6.98 Å and α=β=γ= 90°. The volume of the unit cell is 386$Å^3$. The obtained results for the undoped KDP coincide very well with the reported literature data[17] and from Table No.1 it is evident that the incorporation of Li^{2+} into the crystal lattice of KDP does not change the lattice parameters of KDP and this confirms that Li^{2+} has been incorporated into KDP with complete perfection. The calculated lattice parameters for undoped and Li^{2+} doped KDP crystals are given in Table No.1.

Fourier Transform Infrared spectral analysis

The structural change during crystallization has been studied by FTIR spectroscopy. The FTIR spectra were recorded between the ranges of 400-4000 cm^{-1} using PERKIN ELMER spectrophotometer by KBr pellet technique. Figure No.3a and 3b shows the recorded FTIR spectra of undoped and Li^{2+} doped KDP crystals.

In the spectrum of KDP, there is a broad band in the higher energy region due to O - H stretching vibration of KDP. The absorption band at 3420 cm^{-1} corresponds to P - OH stretching and 2347 cm^{-1} to OH and P - OH stretching. At 1719 cm^{-1} P - O - H bending vibrations are observed. Bands at 1300 cm^{-1} and 905 cm^{-1} corresponds to O - H deformation, P = O stretching and P - O - H stretching HO - P - OH bending respectively. The absorption band at 1100 cm^{-1} corresponds to the P=O stretching. P - OH stretching and HO - P - OH bending vibrations are found at 821 cm^{-1} and 619 cm^{-1} respectively. The bands below 1300 cm^{-1} such as, 1100 cm^{-1}, 905 cm^{-1}, 548 cm^{-1}, 462 cm^{-1} occur due to PO_4 vibrations[18].

In the case of Li^{2+} doped KDP, the peak at 2687 cm^{-1} corresponds to P - O - H stretching, whereas 2352 cm^{-1} corresponds to P – OH and OH stretching, 1689 cm^{-1} corresponds to O = P - OH stretching vibration, 1299 cm^{-1} and 1100 cm^{-1} absorption peaks are attributed to P = O stretching, P - OH stretching and HO - P - OH bending vibrations are found at 835 cm^{-1} 547 cm^{-1} is attributed to HO - P - OH bending vibration. Table No.2 shows the vibrational assignments of undoped and Li^{2+} doped KDP crystals. It can be observed from the Table No.2 that the dopant coordinates with the primary solution at 2352 cm^{-1}.

Optical Transmission Spectral Analysis

A good optical transmittance is desirable property for NLO crystal since the absorptions, if any, in an NLO material near the fundamental or the second harmonic will lead to the loss of conversion efficiency in those wavelengths.

Absorption spectra of NLO material play a major role in device fabrication. Wider the transparency window more will be the practical applicability of that material. The UV-Vis spectrum gives information about the structure of the molecule that the absorption of UV and visible light involves in the promotion of electrons in σ and π orbital from the ground state to higher energy state. The UV transmission spectrum of pure and doped KDP is shown in Figure No.4.The resultant spectrum for undoped and Li^{2+} doped KDP crystals shows that the crystal has very low absorbance in the entire visible and IR region. The lower cut off for pure and Li^{2+} doped KDP is 240 nm. The percentage of transmittance for undoped KDP is 65% and Li^{2+} doped KDP is 75%. This results in a high percentage of transmission which is one of the most desired properties for the crystals that are used in NLO devices[19].

Microhardness Measurements

A number of research articles were proved that the material hardness is related to their constituent

atoms. So, the microhardness studies were carried out on the grown crystals using Vickers microhardness tester attached with an optical microscope. The Vickers microhardness number was evaluated from the relation.

$$H_v = (1.8544 \times p) / d^2 \text{ kg/mm}^2$$

Where p was the applied load in kg and d was the diagonal length of the indentation impression in micrometer. The variations of Vickers hardness number with an applied load of undoped and doped KDP crystals were shown in Figure No.5. The plot indicated that the hardness of the undoped and doped KDP crystal increased with increasing load was also compared to the parent material and the doped one having a greater hardness value. The higher the hardness values, grater was the stress required to form dislocation and also absence of liquid inclusions.

The work hardening coefficient was determined using the relation, $p = kd^n$, k being material's constant, n the Meyer's index[20]. The work hardening coefficient 'n' is found in undoped and Li^{2+} doped KDP crystal by taking the slope of the straight lines of the graph drawn between log p and log according to Onitsch and Hanneman[21,22], n should be between 1 and 1.6 for hard materials and above 1.6 for softer ones. The value of the work hardening coefficient (n) of undoped and Li^{2+} doped KDP crystal was found to be more than 1.6. Hence the grown crystals belong to the soft material category and hence fitting as good engineering material for device fabrication.

Second Harmonic Generation Test

The grown undoped and Li^{2+} doped KDP single crystals were subjected to Kurtz powder second harmonic generation test to study their NLO efficiencies. The crystalline powder was illuminated using an Nd: YAG laser using first harmonic output of 1064 nm with a pulse width of 10 ns and a repetition rate of 10 Hz. The second harmonic signal generated in the crystalline samples were confirmed from the emission of green radiation of wavelength 532 nm collected in a monochromator after separating the 1064 nm pump beam with an IR blocking filter. A photo multiplier tube was used as a detector. It was observed that the measured second harmonic generation efficiency of Li^{2+} doped KDP crystal was 1.6 times that of undoped KDP, which was used as a reference sample. Table No.2 shows the comparison of SHG efficiencies undoped and Li^{2+} doped KDP[23].

Surface Morphology and Compositional Analysis

The SEM micrographs were obtained in various resolutions and magnifications using HITACHI model SEM equipped with EDX. The SEM micrographs of Li^{2+} doped KDP crystals are shown in Figure No.6a-d. From the SEM micrographs it is evident that the particles are evenly distributed. Li^{2+} doping does not alter the surface morphology of the KDP crystal. The presence certain microstructural defects can also be seen clearly in Figure No.6d. Since the particles are closely packed in the SEM micrograph it is evident that the title material possesses good electrical conductivity. The presence of Li^{2+} in the crystal lattice of KDP crystal is confirmed by EDX analysis. The EDX pattern which confirms the doping of Li^{2+} in KDP crystal.

Thermal analysis

Thermogravimetric (TG) and Differential thermal (DA) analyses of the grown crystals were studied by using EXSTAR 6200 thermal analyzer at a heating rate of 20°C/min in nitrogen atmosphere thermal analysis was carried out between the range of 25°C and 1200°C. The TG and DTA curves of Li^{2+} doped KDP crystals are shown in Figure No.7. Continuous loss of the mass of the grown crystals which makes 13-15% is observed at temperatures up to 390°C. The TG curve has three sections corresponding to the temperature ranges of 30-200°C, 200-350°C and 350-1000°C. For the first and the third sections the mass loss is insignificant and caused by removal of the adsorbed water and of the residual products of dehydration and a weight loss was occurred at 390°C without any intermediate stages which corresponds to the melting point of the material. Since there is no weight loss occurred in this stage and it may be confirmed that no water was absorbed by the compound. From the DTA analysis, the two major endothermic peaks are occurred such as 250°C and 290°C. This temperatures range that corresponds to dehydration of the crystals[24,25]. These two endothermic peaks indicate the two different stages of decomposition of the grown crystals.

Table No.1: Lattice parameters of undoped and Li^{2+} doped KDP crystals

S.No	Lattice parameters	Undoped KDP Reported value [17]	Undoped KDP present work	Li^{2+} doped KDP
1	a	7.44 Å	7.46 Å	7.49 Å
2	b	7.44 Å	7.46 Å	7.49 Å
3	c	6.96 Å	6.97 Å	6.98 Å
4	α	90°	90°	90°
5	β	90°	90°	90°
6	γ	90°	90°	90°
7	Volume	383.53 $Å^3$	385 $Å^3$	386 $Å^3$
8	Space group	I42d	I42d	I42d
9	System	Tetragonal	Tetragonal	Tetragonal

Table No.2: Vibrational assignments of undoped and Li^{2+} doped KDP

S.No	Wave number undoped KDP cm^{-1}	Wave number Li^{2+} doped KDP cm^{-1}	Tentative assignments
1	3420	2685	P – OH stretching
2	2347	2352	O – H and P – OH stretching
3	1100	1155	P=O stretching
4	905	835	P – OH stretching and HO – P – OH bending
5	548	547	HO – P – OH bending

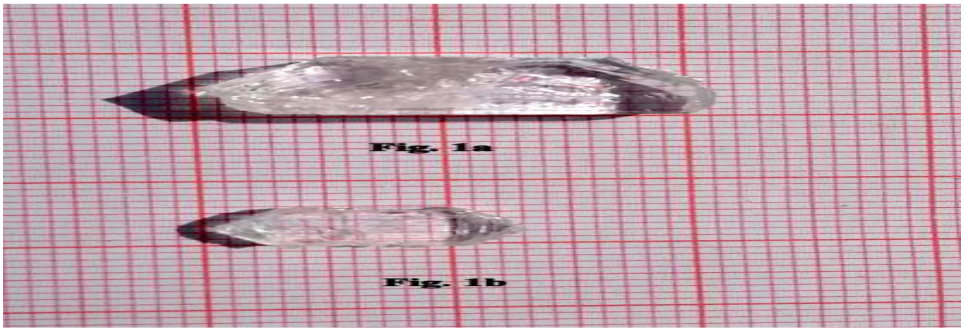

Figure No.1a and 1b: As grown pure and Metal doped KDP crystal

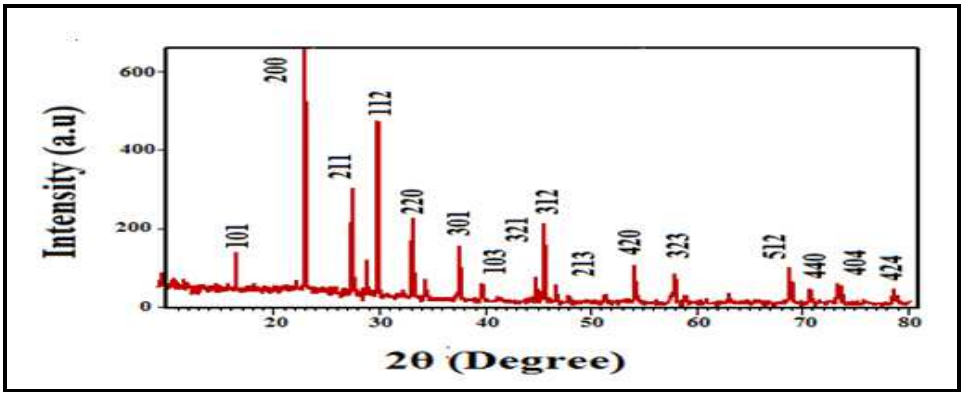

Figure No.2a: Powder XRD pattern of KDP crystal

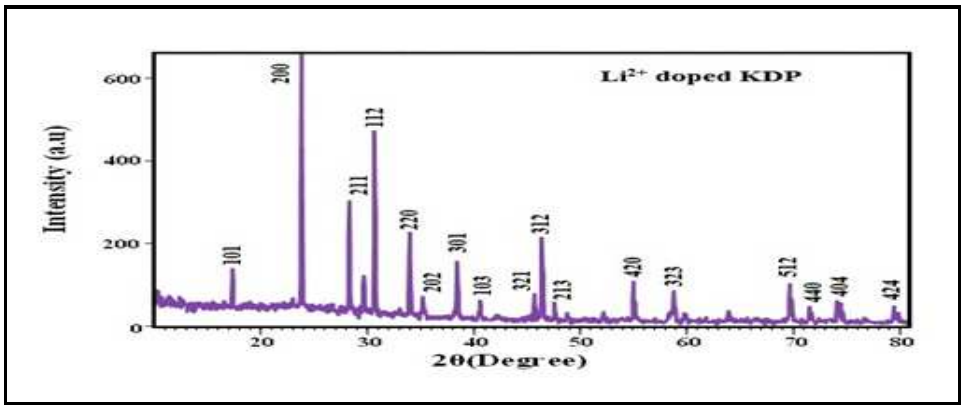

Figure No.2b: Powder XRD pattern of Metal doped KDP crystal

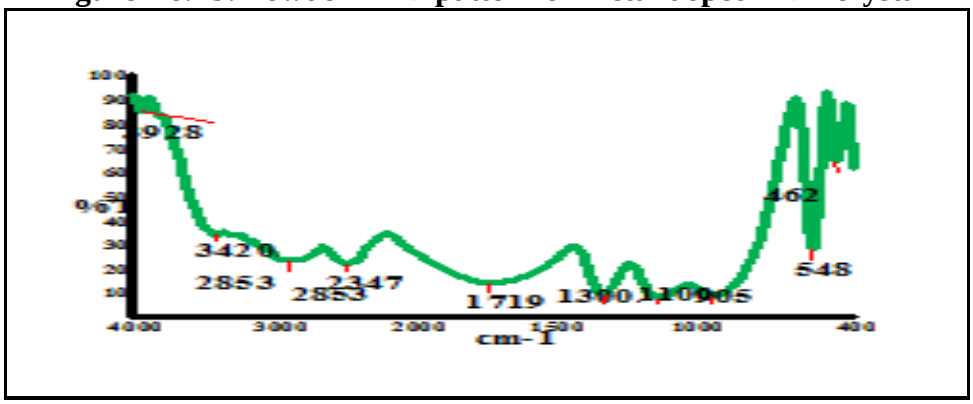

Figure No.3a: FTIR spectrum of undoped KDP crystals

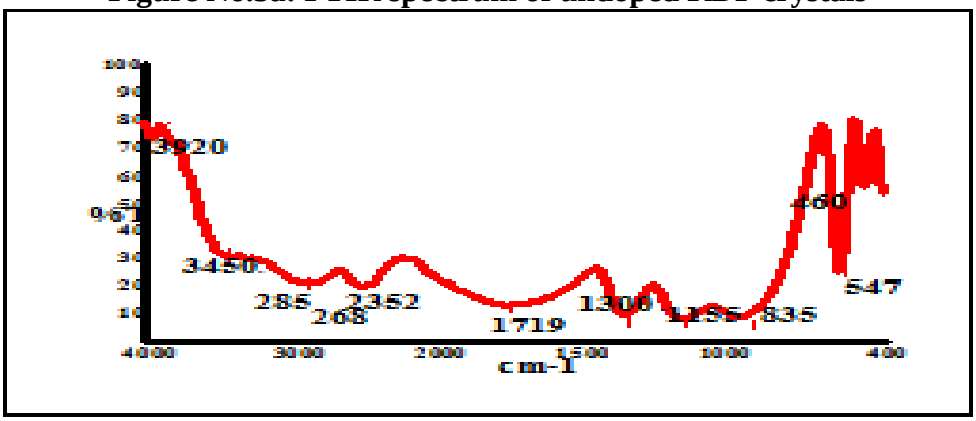

Figure No.3b: FTIR spectrum of metal doped KDP crystals

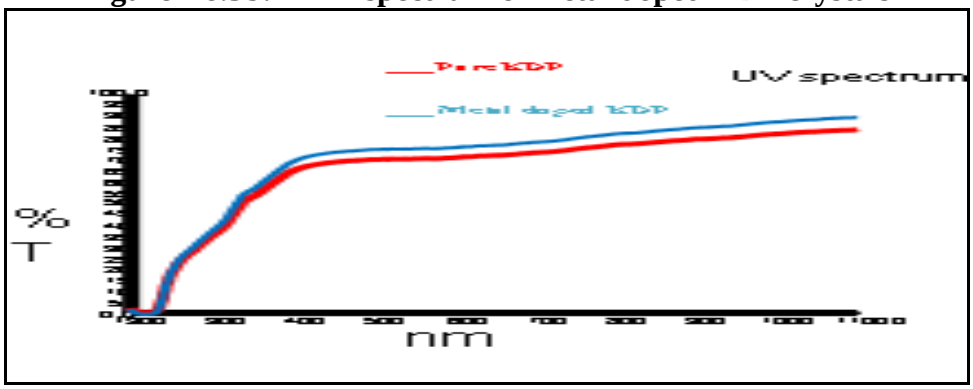

Figure No.4: UV transmission spectrum of pure and metal doped KDP

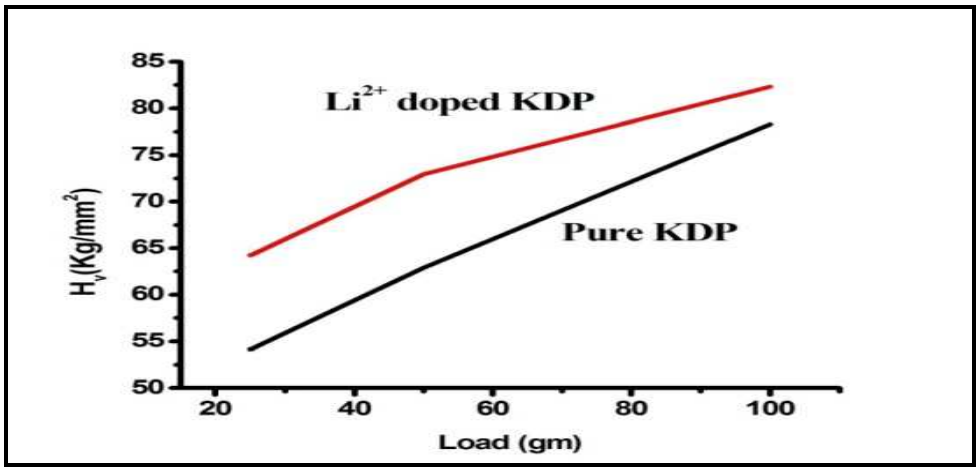

Figure No.5: Vickers Hardness number with loads for undoped and Li^{2+} doped KDP crystals

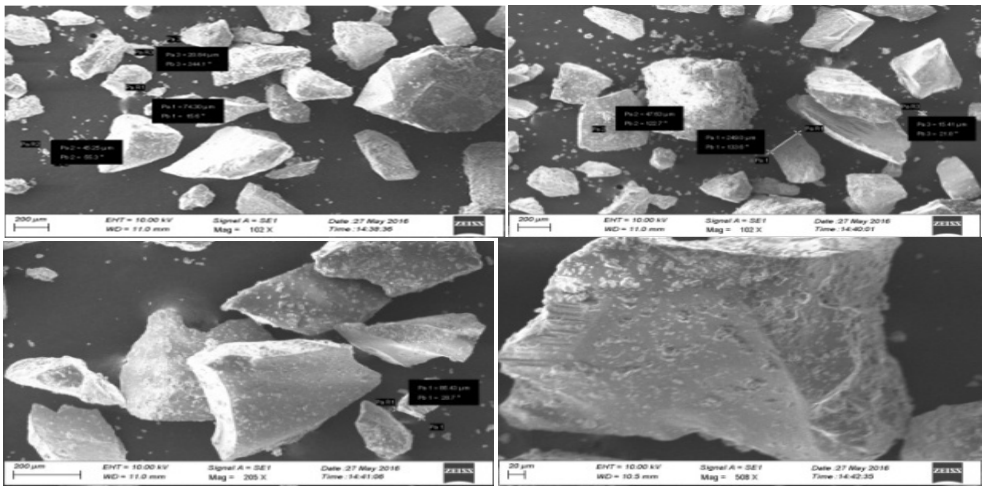

Figure No.6: (a)-6(d): SEM micrograph of Li^{2+} doped KDP crystal

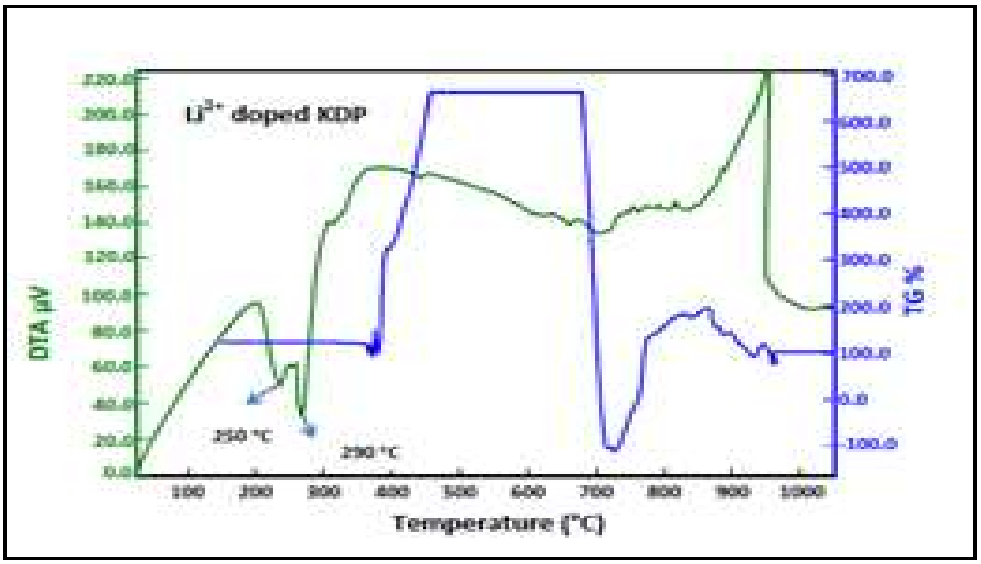

Figure No.7: TG and DTA curves of Li^{2+} doped KDP crystals

CONCLUSION

Undoped and Li^{2+} doped KDP single crystals were grown from Slow evaporation solution technique. The grown single crystals were subjected to various characterization techniques. The structural characters and lattice parameters were assessed by single crystal XRD and the crystal was found to crystallize on tetragonal system with the space group I42d. Spectral characters and the presence of functional groups were determined by FTIR spectral analysis. Linear Optical studies and the optical characters of the samples were analyzed by UV - Vis Spectral analysis and it was found that the samples were transparent in the entire visible region. Also it was found that Li^{2+} doped KDP crystal has a greater transmittance value than the undoped KDP crystal. SEM micrographs show the uniform distribution of particles on the crystalline surface. The substitution of Lithium ion in the crystal lattice of KDP crystal was confirmed by EDX analysis. The enhancement of the thermal decomposition temperature to 250°C makes the material an eligible candidate for laser applications. Mechanical stability of the sample was evaluated by Vicker's microhardness test which reveals that Li^{2+} doped KDP single crystals has a greater hardness value than undoped KDP. SHG efficiency test confirms that Li^{2+} doped KDP has an efficiency of 1.6 times than that of undoped KDP. From these investigations it can be concluded that the title Li^{2+} doped KDP single crystals are potential candidates for fabrication in Optical devices.

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CONFLICT OF INTEREST

We declare that we have no conflict of interest.

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