

Remarkable Effect of Alkali Metal Doping on the Properties of Potassium Hydrogen Phthalate Single Crystals for Optoelectronic and Nonlinear Optical Applications

S. Shek Dhavud¹ and J. Thomas Joseph Prakash²

¹PG and Research Department of Physics, Jamal Mohamed College (Autonomous),
Affiliated to Bharathidasan University, Trichy, Tamilnadu, India

²PG and Research Department of Physics, Government Arts College, Affiliated to Bharathidasan University,
Trichy, Tamilnadu, India

ABSTRACT

This present investigation reports the impact of alkali metal, for example, Cesium (Cs) doping on the properties of potassium hydrogen phthalate (KHP) crystals were grown by means of slow evaporation solution growth technique. The XRD and FT-IR analyses imply that the crystal undergoes extensive stress because of doping. The decrease in the peak intensity for the particular plane of (130) observed in powder XRD for Cs doped crystal and slight modifications in vibrational frequencies show minor structural variations. The optical examinations were investigated by UV-Vis-NIR analysis and show high optical transparency in the doped sample. The photoluminescence analysis of the grown crystals was investigated. Surface morphological changes owing to doping are ascertained by SEM and addition of the Cs dopant into KHP crystal lattice was well affirmed by energy dispersive X-ray spectroscopy (EDAX). TG/DTA examination reveals the purity of the materials and no decomposition is seen up to the melting point. The remarkable enhancement in mechanical strength was ascertained owing to doping by Vicker's microhardness test. It's observed that the doping with the low concentration of alkali metal facilitates nonlinearity and enhances the second harmonic generation (SHG) efficiency to a noteworthy extent.

Keywords: Optical materials, SEM, EDAX, NLO.

I. INTRODUCTION

Potassium hydrogen phthalate (KHP) is supported as the model compound attributable to its all-around created surface example on the (010) face comprising of high and very low growth steps which may be comparatively effortlessly observed by means of optical microscopy [1,2]. KHP may be a polar crystal (point group mm2) and we utilized KHP in a further endeavor to prepare self-frequency doubled single crystal dye lasers that we did no longer succeed in fashioning from KDP. The inclination of KHP crystals to delaminate under high power laser illumination was a constraining factor. However, KHP was utilized to exhibit the two-photon light of enclosed dyes [3,4]. The inclination to delaminate is related with KHP's ideal (010) cleavage. This feature supported a method for testing whether crystals may transfer data starting with one generation

onto the next by cleavage and growth,[5] a thought initially enunciated by Cairns-Smith who trusted that the primary genes needed to be stable and abundant on the prebiotic earth [6]. Impact of various sorts of additives on spiral growth phenomena on (010) KHP specifies the presence of various mechanisms of interaction.

It is outstanding that additives impact the mechanical, electrical, electronic, optical properties and surface morphology relying upon the nature of host material and the additive [7-10]. In the current past, the scientists have announced a few significant investigations on the impact of doping in nonlinear optical materials which improved the crystalline perfection monitored by the enhancement of SHG efficiency [7,8]. It has additionally been set up that especially the metal ion additives are the most versatile in modifying the

properties of a compound [11,12]. The inclusion of a few amounts of impurities in the form of alkali metals plays a vital role in KHP crystal has studied [13, 14].

In this present work, assessing the impact of Cs doping on various key properties of KHP crystals, we have characterized them by various methods, for example, single and powder XRD, FT-IR, UV-Visible-NIR, photoluminescence, SEM/EDAX, TG/DTA, mechanical and SHG properties of undoped KHP single crystal with addition of cesium as a dopant and propose it as a superior possibility for optoelectronic applications.

II. EXPERIMENTAL DETAILS

2.1. Synthesis and crystal growth

The undoped and doped crystals were grown by way of a slow evaporation solution growth technique (SEST). A saturated aqueous solution of Potassium hydrogen phthalate (E-Merck) was readied (12 g per 100 ml). Cs as Cesium nitrate (CsNO_3) was utilized. 0.5 mole % of CsNO_3 was brought into the aqueous growth medium as an additive. Saturated solutions of undoped and CsNO_3 doped KHP were prepared. Once filtration, it absolutely was preheated to 5°C above the saturation temperature and left for 1 hour under stirring to ensure homogeneity and afterward, the tightly covered saturated solution with a Whatman filter paper was kept in a constant temperature bath. The crystallization occurred within 15–21 days and the incredibly obvious crystals have been obtained from the aqueous growth medium. Highest quality and extremely transparent crystals are utilized in the preparation of bulk crystals. It absolutely was visually remarked that the growth rate of crystals was high with low additive concentration. Photographs of undoped and Cs doped KHP as grown crystals are depicted in Fig. 1(a) and (b).

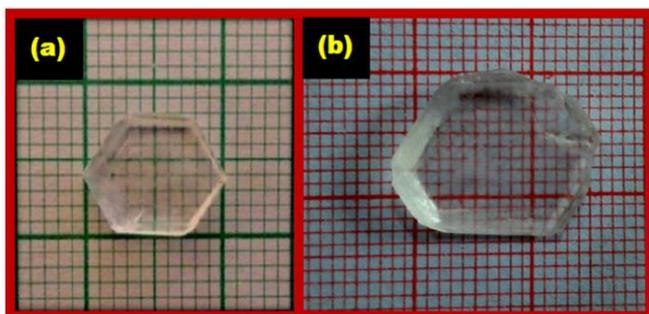


Figure 1 : As grown crystals of (a) Undoped (b) Cs doped KHP

2.2. Characterization techniques

The single crystal XRD analysis of undoped and Cs doped KHP crystals was indicated by using ENRAF NONIUS CAD 4 diffractometer with $\text{MoK}\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$) to identify the unit cell parameters. Powder X-ray diffraction pattern of the grown crystals was recorded on X'pert PRO powder X-ray diffraction (40 kV) using $\text{Cu-K}\alpha$ radiation of wavelength $\lambda = 1.5406 \text{ \AA}$. The presence of functional groups, absorption peaks and the tentative bond assignments, nature of the bonds present in the undoped and metal doped KHP crystals were assessed by FT-IR spectral analysis using PERKIN ELMER RXI FTIR spectrophotometer. The UV-Vis-NIR transmittance spectra of undoped and Cs doped crystals recorded in the range of 190–1100 nm using PERKIN ELMER LAMBDA 35 UV-Visible spectrophotometer. Photoluminescence emission spectra of the grown crystals were recorded using a Perkin Elmer LS-55 spectrometer. The scanning electron microscope (VEGA3 TESCAN) equipped with energy dispersive analytical X-ray unit (EDAX) was used to study the surface morphology and the presence of the dopant in the grown crystals. In the present investigation, the simultaneous TG/DTA of undoped and Cs doped KHP crystals were observed using a Perkin-Elmer thermal analyzer STA 409 PC in the nitrogen atmosphere under 1000°C at a heating rate 20 K/min . Vicker's microhardness measurements have applied the utilization of Leitz Weitzler hardness tester fitted with a diamond indenter. In order to confirm the influence of doping on the NLO properties, undoped and Cs doped KHP crystals have been subjected to a Q-switched Nd:YAG laser beam of wavelength 1064 nm was hired within an input beam energy of 3.2 mJ/pulse and pulse width of 8 ns , the repetition rate being 10 Hz and KDP was taken as the reference material.

III. RESULTS AND DISCUSSION

3.1. FT-IR analysis

The FT-IR spectra of undoped and Cs doped KHP crystals were recorded within the wave number range of 400 cm^{-1} and 4000 cm^{-1} (Fig. 2). From Fig. 2, it exhibits that the doping of KHP crystal lattice typically provides rise to a slight shift in a number of the characteristic vibrational frequencies. For the undoped KHP crystal, a carbonyl group ($\text{C}=\text{O}$) was ascertained around 1673 cm^{-1} . C-H stretching vibrations found at 2780 cm^{-1} and aromatic ring groups seem at 1562 cm^{-1} . The C-OH in-

plane and out of plane bands were seen as weak bands at 1483 cm⁻¹ and 952 cm⁻¹ respectively. Carboxylic O-H stretching vibration was ascertained to make multiple bands near 3528 cm⁻¹ and absorption band in the region which is less than 900 cm⁻¹ seems due to C-H bending vibrations. Similarly, For Cs doped KHP, a carbonyl group (C=O) was seen around 1679 cm⁻¹. C-H stretching vibrations occur at 2785 cm⁻¹ and aromatic ring groups found at 1564 cm⁻¹. The C-OH in-plane and out of plane bands were ascertained as weak bands at 1486 cm⁻¹ and 959 cm⁻¹ respectively. Carboxylic O-H stretching vibration is seen to make multiple bands near 3555 cm⁻¹. The modification in the position of O-H absorption band could be owing to the partial cesium substitution for potassium in the KHP crystal. A considerable shift in some of the characteristic vibrational frequencies of undoped KHP is ascertained owing to doping with Cs. Vibrational band assignments of undoped and Cs doped KHP crystals are presented in Table 1.

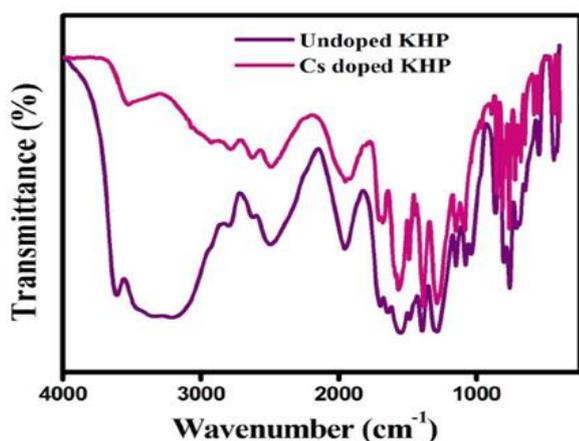


Figure 2 : FTIR spectrum of undoped and Cs doped KHP crystals

Table 1: FTIR vibrational frequencies of undoped and Cs doped KHP crystals

Undoped KHP (cm ⁻¹)	Cs doped KHP (cm ⁻¹)	Vibrational band assignments
3528	3555	O-H stretching hydrogen bond
2780	2785	C-H stretching
1673	1679	C=O stretching
1483	1486	C-O-H in plane
952	959	C-O-H out of plane
905	910	C-H bending

3.2. Powder X-ray diffraction analysis

The powder XRD analysis of undoped and doped KHP crystals shows that the grown crystals are of a single phase without a detectable impurity. The sharpness of the prominent peaks indicates the high crystallinity of the title compound. At room temperature all the observed reflections were indexed and the indexed powder XRD pattern is presented in Fig.3.

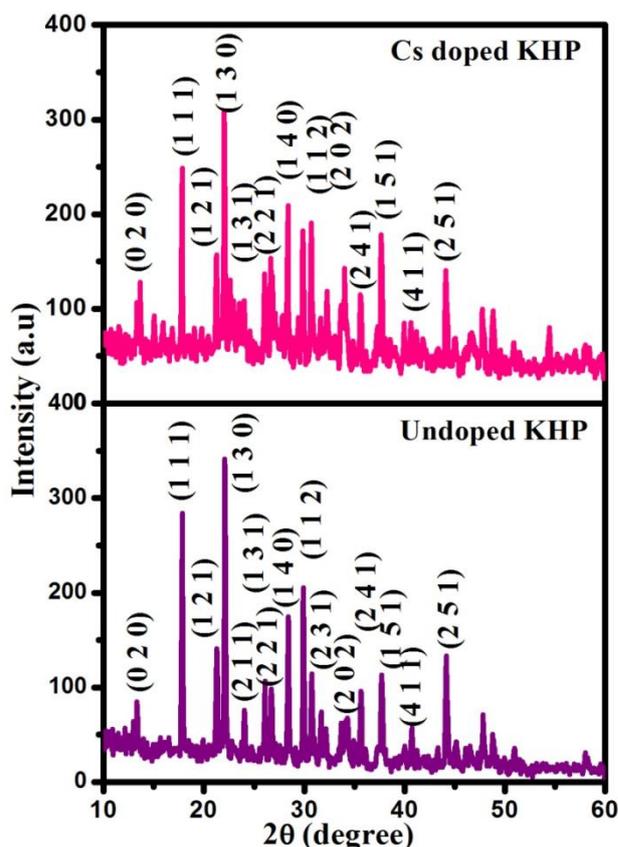


Figure 3 : Powder XRD pattern of undoped and Cs doped KHP crystals

Assessing the impact of Cs doping on peak position we have focused on the prominent peaks which evidently depicts that the intensity of the prominent peaks has been decreased compare to undoped one and these observations could be attributed to strains in the KHP crystal lattice due to the doping.

Estimation of crystallite size by Scherrer analysis

The crystallite size of undoped and doped KHP crystals was determined by the Scherrer equation

$$D = \frac{k\lambda}{\beta_D \cos \theta} \quad \text{----- (1)}$$

Where D is the volume weighted crystallite size (nm), k is the shape factor (k = 0.9), λ is the wavelength of the X-rays (k = 1.54056 Å for Cu Kα), θ is Bragg diffraction angle and β_D is the Full width at half-

maximum intensity (FWHM) in radians. The crystallite size of undoped and doped KHP crystals was determined as 23.54 nm and 19.68 nm respectively.

3.3. Single crystal X-ray diffraction analysis

From the single crystal XRD analysis, undoped and doped KHP crystals crystallize in orthorhombic system with space group $Pca2_1$ which evidently indicates that doping does not disturb the structure of the crystal but only morphology. The results of the unit cell parameters for Cs doped KHP crystal is compared with the reported literature data of pure KHP [15, 16]. The unit cell parameters for undoped and doped KHP crystals are presented in Table 2. The doping of Cs ion in the undoped crystal which decreases the crystal lattice owing to the presence of the interstitial spaces and as well the development of local compressive strain in the lattice [17]. The slight variation is observed in the values of the lattice parameters of the grown crystals due to the presence of Cs ion in KHP crystal.

Table 2: Values of unit cell parameters for undoped and Cs doped KHP crystals

	Undoped KHP	Cs doped KHP
Unit cell parameters	a=6.56Å	a=6.41Å
	b=9.60Å	b=9.53Å
	c=13.38Å	c=13.30Å
	$\alpha = \beta = \gamma = 90^\circ$	$\alpha = \beta = \gamma = 90^\circ$
Volume V (Å ³)	842.61	812.46
Crystal system	Orthorhombic	Orthorhombic
Space group	$Pca2_1$	$Pca2_1$

3.4. Linear optical analysis

The extensive optical transparency range of single crystals plays a very significant role in optoelectronic device preparation. Therefore, it's important to grow a good quality, defect-free crystals for numerous applications. So as to avoid the intrinsic defects, several researchers attempt to dope pure materials with additives, especially alkali metals additives [13,14]. Consequently, assessing the impact of doping on optical

properties of KHP crystals we have recorded the optical transmission spectra of undoped and doped KHP crystals as depicted in Fig. 5. From Fig. 5, it is explicit that the optical transparency of the grown crystals is quite good in the entire examined wavelength region. The optical transparency of undoped and Cs doped KHP crystal is observed to be ~70% and ~90% respectively. The essential UV-Visible cut-off wavelength is remarked to be at 300 nm for undoped and doped KHP crystals. No significant λ_{max} shift is observed however the absorbance is diminished drastically by doping. Owing to high transparency, the doped crystal is very valuable for optical device applications.

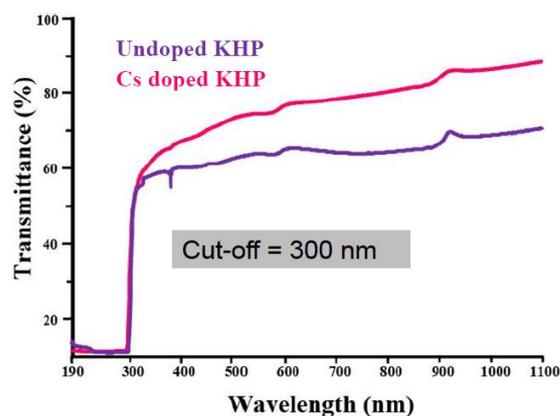


Figure 5: UV-Visible Transmission spectrum of undoped and Cs doped KHP crystals

3.5. Photoluminescence studies

Photoluminescence emission spectra of the grown crystals were recorded at room temperature with the excited wavelength of 300 nm indicated in Fig. 6(a) and (b). It is widely recognized that the grown crystals display intriguing photoluminescence (PL) properties indicating strong and abroad emission bands in the UV-Visible range. In the solid state, ligand-ligand interactions are imperative for applications that include charge transport and to acquire tunable emission colors [18]. The PL emissions are recorded for undoped and Cs doped KHP crystals covering from the very short wavelength of 325 nm to long wavelength 550 nm. The recorded spectra fitted by Gaussian function with five peaks for both undoped and doped KHP crystals. The solid lines represent the linear combination of five Gaussian peaks where 340 nm has the lowest for both undoped and doped KHP crystals and 506 nm and 509 nm have the highest wavelengths for undoped and doped KHP crystals respectively. The consequences of this investigation show an extreme photoluminescence in the violet-green spectral region.

The PL emission spectra of undoped and Cs doped KHP crystals are having five peaks at (340, 426, 460, 480 and 506 nm) and (340, 408, 435, 466 and 509 nm) respectively. These groups are violet emission, blue emissions and green emission respectively. Undoped KHP has no violet emission; an extreme wide violet emission band seemed in the range 408 nm for Cs doped KHP. The blue emission wavelength values of Cs doped KHP (435 and 466 nm) increments when contrasted with undoped KHP (426, 460 and 480 nm). This blue shift may arise from various roots, for example, electron-phonon coupling, lattice distortion, localization of charge carriers owing to interface impacts and point defects. There is one green emission band at 506 nm and 509 nm for undoped and Cs doped KHP respectively. The Cs doped KHP crystal green emission values likewise increment when contrasted with undoped KHP. This is owing to the Cs ion dopant impacts into the KHP lattice sites.

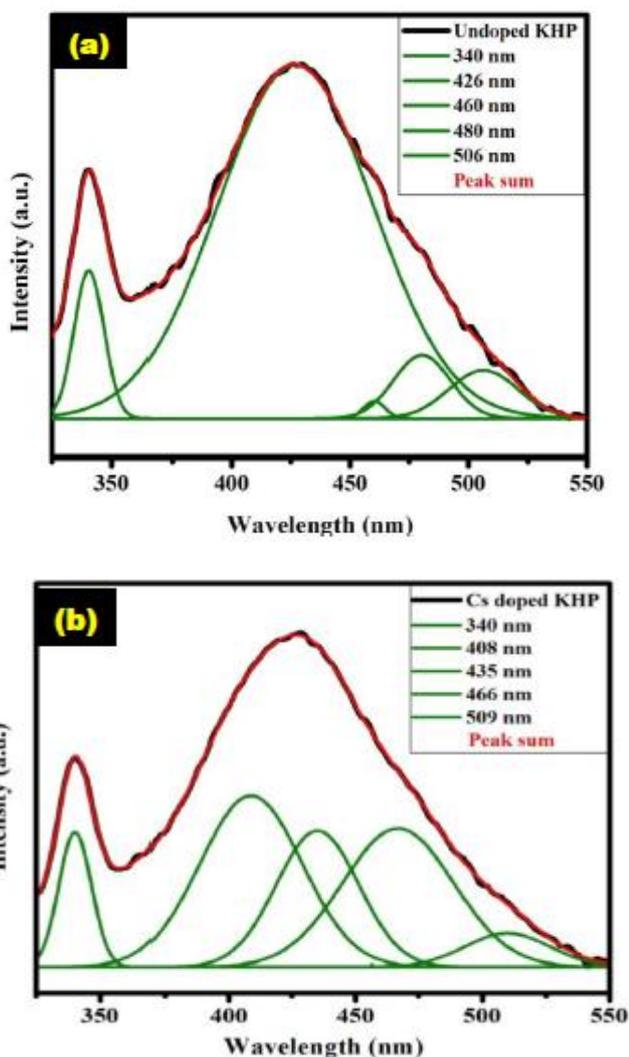
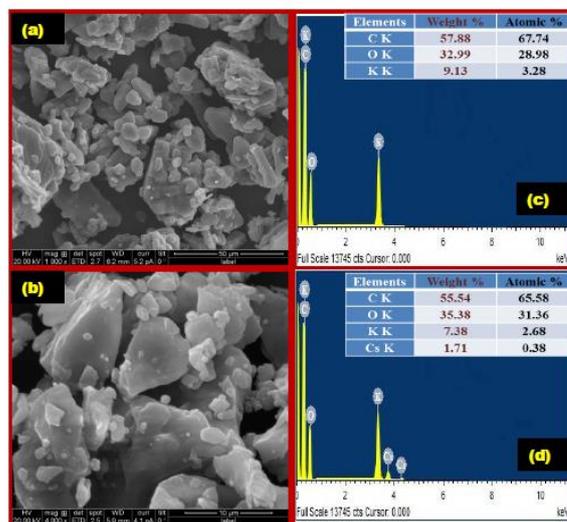


Figure 6 : Photoluminescence spectrum of (a) Undoped KHP crystal (b) Cs doped KHP crystal

3.6. SEM and EDAX analysis

Fig. 7(a) and (b) demonstrates the SEM images of as grown single crystals of undoped and doped KHP crystals. The Cs doped KHP crystal exhibits the grain size of the order of few micrometers on the surface (10 μm) which are uniformly distributed than undoped KHP crystal whereas the grain size of the undoped KHP (50 μm). The substitution of metal ion inside the KHP lattice induces the distortion which is chargeable for grain size reduction. Tensile stress is totally relieved and the lattice is much relaxed which makes better crystallization. The presence of agglomerated particles proposes that the growth process begins with groups in a colloidal state. These clusters coordinate into larger particles called secondary spherical particles. This limits their surface energy. It is explicit from the investigations that the doping modifications the morphology, subsequent in crystal voids. The results obtained in the present work coincide well with the powder X-ray diffraction analysis (section 3.2).

The inclusion of metal ion into the crystalline matrix of KHP was affirmed by EDAX analysis. The percentage of Cs is explicit in the EDAX spectra as shown in Fig. 7(c) and (d). From Fig. 7(c) and (d), the presence of C, O and K extreme peaks are present which shows the formation of Cs doped KHP single crystal. In examination with undoped KHP, it is observed that the EDAX which specifies the inclusion of Cs ion in the crystal lattice of KHP indicated in Fig. 7(c) and (d). It reveals that the accommodating capability of the host crystal is limited and only a small quantity is incorporated into the crystalline matrix.



3.7. Thermal Analysis

The absence of water of crystallization inside the molecular structure is showed by the absence of weight loss around 100 °C. Thermal stability of the doped specimen is slightly increased by way of doping with Cs (300 °C) in the examination with the thermally stable temperature for undoped KHP (290 °C) is indicated in Fig. 8(a) and (b). The result obtained in the present work agrees well with the results reported [19, 20]. These authors investigated the thermal behavior of KHP in nitrogen (N₂) and air atmospheres. In a nitrogen atmosphere, these authors reported that Potassium carbonate and char were occurred by decomposition of KHP at 800 °C. From the DTA analysis, it is explicit that the slight addition in temperature is evident for the doped crystal, suggesting that the substitution of Cs ions enhanced the thermal stability of undoped KHP which affirms that cesium is doped into the crystal lattice of KHP. No decomposition up to the melting point ensures the suitability of the material for utility in lasers wherein the crystals are required to withstand high temperatures.

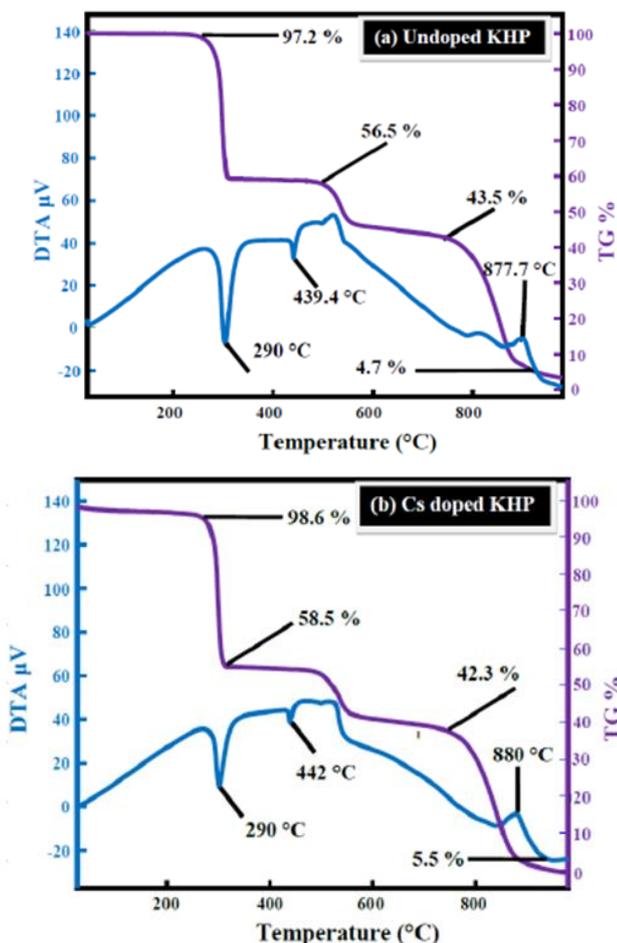


Figure 8 : TG/DTA curves of (a) undoped KHP crystals (b) Cs doped KHP crystal

3.8. Mechanical Analysis

The structure and molecular composition of the crystals are immensely related to the mechanical hardness. It is vital to perceive the mechanical strength of the grown crystals because it plays a key role in devices. Additionally, the hardness is one of the fundamental physical characteristic of any material to comprehend its plasticity and the strength in pure as well as doped form. The hardness of the crystal also relies upon at the kind of chemical bonding, the presence of dopants and nature of the material. It is characterized much simple resistance offers to the motion of dislocations [21], as the capacity of a crystal resists a structural breakdown under applied stress [22]. Among different microhardness tests, the Vickers hardness is one of the vital deciding factors in selecting processing cutting, grinding and polishing) steps of bulk crystal in the fabrication of devices based crystal [23]. The variation of Vickers hardness number (Hv) as a function of applied loads (25 g, 50 g and 100 g) of undoped and Cs doped KHP crystals is depicted in Fig. 9. From Fig. 9, obviously, the hardness value increases with increasing load, thus satisfying the normal indentation impact. In this association, the present investigations indicate Hv values of doped crystal are high contrasted with the undoped crystal. The higher Hv value for Cs doped KHP correlates well with its higher thermal stability as revealed by thermal analysis (Section 3.7). The explanation behind the higher hardness in the doped crystals could be comprehended viz., the addition of the monovalent impurity (Cs) has an appreciable impact on the hardness of ionic crystals. The real commitment to the increment in hardness is ascribed to the high stress required for homogeneous nucleation of dislocation in the small dislocation free region indented [24]. Hence, the higher hardness value in the present examination is because of surface hardening impact due to the incorporation of Cs additive and also to the absence of micro-growth layers and liquid inclusions. According to Meyer's law, the relationship between load and size of the indentation is given by

$$P = k_1 d^n \quad \text{----- (2)}$$

Where P is the load applied (kg), d is the diagonal length of impression (mm), k₁ is a constant and n is Meyer's index or work-hardening coefficient.

From the slope of log P vs log d plots depicted in Fig. 10(a) and (b), n values is estimated by the least square fitting method for undoped (2.30) and Cs doped KHP (3.20). The value of work-hardening coefficient (n) comes out be 1-1.6 for hard materials category and more than 1.6 for soft ones. Thus the present crystals under examination belong to a soft material category.

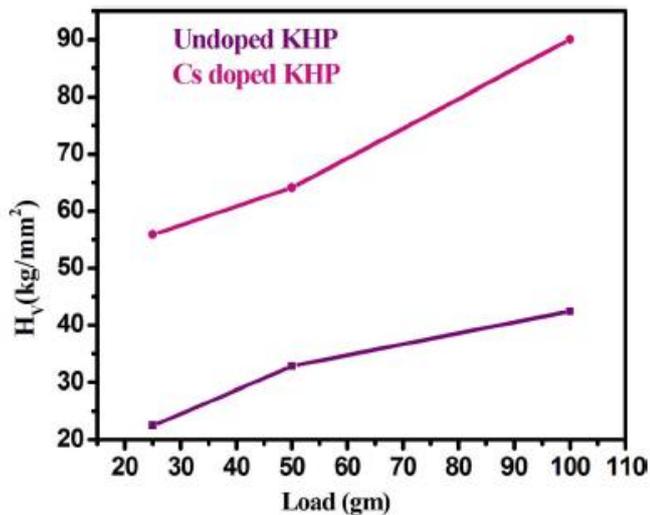


Figure 9: Load vs Hv for undoped and amino acid doped KAP crystals

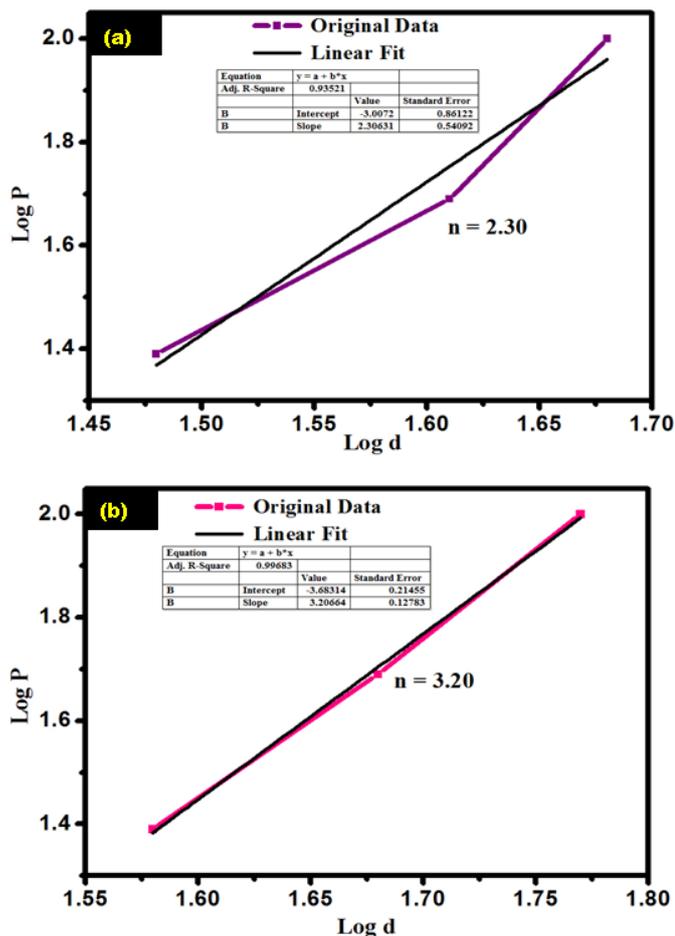


Figure 10: Log P vs Log d plot of (a) undoped KHP crystal (b) Cs doped KHP crystal

3.9. SHG efficiency

The output SHG intensities of undoped and doped KHP crystals give the relative nonlinear optical efficiencies. The relative measured the nonlinear optical output of undoped and Cs doped KHP was 1.5 and 1.9 times with respect to KDP respectively. SHG output is increased significantly in the case of the relatively Cs doped KHP crystals. However, a slight improvement of SHG efficiency at a low doping level of Cs could be due to the effortless of charge transfer and hence cesium is a useful dopant. The efficient SHG demands specific molecular alignment of the crystal facilitating nonlinearity.

IV. CONCLUSION

We have utilized XRD, FT-IR, UV-Vis-NIR, PL, SEM/EDS, TGA/DTA, mechanical and Kurtz powder techniques to think about the impact of doping with a light alkaline metal (Cs) on KHP crystals. The single crystal X-ray diffraction revealed that the crystal belongs to an orthorhombic system with noncentrosymmetric space group Pca2₁ and nominal modifications in the cell parameters are observed owing to lattice stress as a result of doping and the results are more noticeable in KHP crystals. Powder XRD demonstrates good crystallinity and intensity variations are seen in view of doping. Correlation of FT-IR of undoped and doped KHP specimens indicates slight shifts in the vibrational pattern owing to the addition of Cs ion in KHP crystal. In the UV-Vis-NIR analysis, the enhancement in optical transmittance reveals that Cs doped KHP crystal has excellent optical quality contrasted with undoped KHP. In PL spectra, the defect level emission of Cs doped KHP crystal was decreased when contrasted with undoped KHP and the optoelectronic properties mainly rely upon the reduction of defect level in material, which influenced by electron-phonon coupling interaction and the outcomes provides strong support for the further improvement of broad optical device application. SEM micrographs reveal that the surface morphology of Cs doped KHP crystal is changed by means of doping. Addition of cesium into the crystalline matrix of KHP is evidenced by EDAX. TG/DTA studies show that doped specimen has higher thermal stability than host material. The hardness value of Cs doped KHP crystal is more noteworthy than that of undoped KHP crystal. The NLO studies show that the presence of dopant slightly enhances the efficiency of undoped KHP. The high

nonlinearity, transparency, thermal stability and mechanical stability reveals that Cs doped KHP crystal is reasonable for optoelectronic and SHG applications.

V. REFERENCES

- [1]. W. J. P. Van Enckevort, L. A. M. J. Jetten, Surface morphology of the {010} faces of potassium hydrogen phthalate crystals. *J. Cryst. Growth.* 60, 275-285 (1982).
- [2]. G. R. Ester, R. Price, P. J. Halfpenny, An atomic force microscopic investigation of surface degradation of potassium hydrogen phthalate (KAP) crystals caused by removal from solution. *J. Cryst. Growth.* 182, 95-102 (1997).
- [3]. J. B. Benedict, P. M. Wallace, P. J. Reid, S.-H. Jang, B. Kahr, Up-conversion Luminescence in Dye-Doped Crystals of Potassium Hydrogen Phthalate. *Adv. Mater.* 15, 1068-1070 (2003).
- [4]. J. B. Benedict, Ph.D thesis. University of Washington (2007).
- [5]. T. Bullard, J. Freudenthal, S. Avagyan, B. Kahr, Test of Cairns-Smith's 'Crystals-as-genes' hypothesis. *Faraday Discuss.* 136, 231-245 (2007).
- [6]. G. Cairns-Smith, Genetic Takeover. Cambridge University Press, Cambridge, UK (1987).
- [7]. S. Meenakshisundaram, S. Parthiban, N. Sarathi, R. Kalavathy,
- [8]. G. Bhagavannarayana, Effect of organic dopants on ZTS single crystals. *J. Cryst. Growth.* 293, 376-381 (2006).
- [9]. G. Bhagavannarayana, S. Parthiban, S. Meenakshisundaram, Enhancement of crystalline perfection by organic dopants in ZTS, ADP and KHP crystals as investigated by high-resolution XRD and SEM. *J. Appl. Crystallogr.* 39, 784-790. (2006).
- [10]. G. Bhagavannarayana, S. Parthiban, Subbiah Meenakshisundaram, An Interesting Correlation between Crystalline Perfection and Second Harmonic Generation Efficiency on KCl and oxalic acid doped ADP Crystals. *Cryst. Growth Des.* 8, 446-451 (2008).
- [11]. D. Donkova, J. Pencheva and M. Djarova, Influence of complex formation upon inclusion of Mn(II), Co(II), Ni(II), and Cu(II) in ZnC₂O₄•2H₂O. *Cryst. Res. Technol.* 39, 207-213 (2004).
- [12]. Praveen, N. Vijayan, C. Mahadevan, G. Bhagavannarayana, Effect of impurities on the crystalline perfection of ZTS. *Mater. Manuf. Processes.* 23, 816-822 (2008).
- [13]. N. Kejalakshmy, K. Srinivasan, Growth, optical and electro-optical characterisations of potassium hydrogen phthalate crystals doped with Fe³⁺ and Cr³⁺ ions. *Opt. Mater.* 27, 389-394 (2004).
- [14]. J. Thomas Joseph Prakash, S. Ekadevasena, Effect of alkali halides on the growth, morphology, spectral, optical, thermal and nonlinear optical properties of potassium acid phthalate crystals for frequency conversion applications. *J Mater Sci: Mater Electron.* 28, 7393-7400 (2017).
- [15]. S. K. Geetha, R. Perumal, S. Moorthy Babu, P. M. Anbarasan, Habit modification and improvement in properties of potassium hydrogen phthalate (KAP) crystals doped with metal ions. *Cryst. Res. Technol.* 41, 221-224 (2006).
- [16]. Y. Okaya, The crystal structure of KC₆H₄COOH.COO. *Acta. Cryst.* 19, 879-882 (1965).
- [17]. P. Murugakoothan, R. Mohan Kumar, P.M. Ushasree, R. Jayavel, R. Dhanasekaran,
- [18]. P. Ramasamy. Habit modification of potassium acid phthalate (KAP) single crystals by impurities. *J. Cryst. Growth.* 207, 325-329 (1999).
- [19]. Elena V. Bolyreva, Evgenia N. Kolesnik, Tatyana N. Drebuschak, Hans Ahsbahs, Jon
- [20]. Ares Beukes, Hans-Peter Weber, A comparative study of the anisotropy of lattice strain induced in the crystals of L-serine by cooling down to 100 K by increasing pressure up to 4.4 GPa. *Z. Kristallogr.* 220, 58-65 (2005).
- [21]. M. D. Allendorf, C. A. Bauer, R. K. Bhakta, R. J. T. Houk, Luminescent metal-organic frameworks. *Chem. Soc. Rev.* 38, 1330-1352 (2009).
- [22]. A.E. Newkirk, Renette Laware, Thermogravimetric analysis of potassium hydrogen phthalate. *Talanta.* 9, 169-173 (1962).
- [23]. R. Belcher, L. Erdey, F. Paulik, G. Liptay, A derivatographic study of potassium hydrogen phthalate. *Talanta.* 5, 53-57 (1960).
- [24]. Y.U. Wang, Y.M. Jin, A.G. Khachatryan, Phase field microelasticity theory and simulation of multiple voids and cracks in single crystals and polycrystals under applied stress. *J. Appl. Phys.* 91, 6435-6451 (2002).

- [31]. J. Stephens, T. Gebre, A. Batra, M. Aggarwal, R. Lal, Microhardness studies on organic crystals. *J. Mater. Sci. Lett.* 22, 179-180 (2003).
- [32]. Ganesh, M. Shkir, P. Shekar, K.K. Rao, Indentation studies on $\langle 100 \rangle$, $\langle 001 \rangle$ and $\langle 101 \rangle$ face of ammonium dihydrogen phosphate (ADP) single crystals: A novel nonlinear optical material. *Optik.* 125, 3268-3271 (2014).
- [33]. Gouldstone, N. Chollacoop, M. Dao, J. Li, A.M. Minor, Y. L. Shen, Indentation across size scales and disciplines: Recent developments in experimentation and modeling. *Acta Mater.* 55, 4015-4039 (2007).