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Synthesis, Crystal Growth and Characterization of Bismuth Doped Potassium Hydrogen Phthalate Crystal (Khp): A Nlo Material

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Abstract

To create single crystals using the Slow Evaporation Solution Growth Technique (SEST), equimolar composition of the transition metal (Bi) as Bismuth nitrate is added to Potassium Hydrogen Phthalate (KHP) (1:1) at ambient temperature. The following analysis is then performed on the single crystals that have formed. Equimolar doping-induced structural distortion in the crystals is confirmed by the FT-IR Spectra. The TGDTA study reveals the purity of the material and no decomposition is observed up to the melting point. Presence of Bismuth is confirmed by Energy dispersive X-ray spectroscopy (EDS). SEM reveals some changes in surface morphology due to doping. The relative intensities of peaks are reduced compared to pure one which may be due to doping of Bismuth to KHP in Powder X-ray diffraction. The values of doped Crystal is reduced compared to pure one. From this single crystal XRD values we can say that the dopant can enter into KHP crystalline matrix and cause slight distortion in it. Due to its high transmittance and absorption in the visible region, it is widely used for optical window application with lower cut off wavelength at 244 nm and 301nm revealing better NLO of the doped crystal then pure one. The doping results insignificant enhancement of (SHG) second harmonic generation resulting in morphological changes.

Keywords: Powder X-ray diffractometer, single crystal X-ray diffractometer, SEM-EDS, slow evaporation method(SEST), nonlinear optics,

INTRODUCTION

Recently potassium hydrogen phthalate has got a wide application in the production of crystal analyzer for long wave X-ray spectrometer [12]. Being a good nonlinear optical material, KHP possess piezoelectric, pyroelectric and elastic properties [3-5]. KHP has been used as substrates for the growth of highly oriented films of Conjugated polymers with nonlinear optical susceptibility [6,7]. Deposition of thin films of NLO materials, like urea with high mechanical stability [8]. Potassium hydrogen phthalate with electro-optical application belongs to an orthorhombic system with space group *Pca*21 [9].The investigation of Fe/Ce impurity effect on KHP is made [10]. A detailed study is made on the surface morphology and the growth kinetics of KHP [11]. The depression of SHG efficiency owing to the deterioration of crystalline perfection is made by Os (VIII) doping on KHP [12]. The thermal and optical properties of Zn doping on KHP crystals is investigated [13].

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The structure and optical properties of amino acid doped KHP crystals is recently discussed [14]. In our present study we have chosen the ’p’ block metal bismuth (Bi) as impurity to our NLO material KHP. Our researchers have made a no of studies on the doping effects of Bi and they are the crystal growth and characterization of Bi crystal growth and characterization of Bi CdxTe [15]. The thermoelectric properties of Ge(Bi,Sb)4Te7 [16] and Bi-Sb-Te [17] are the latest studies on Bi metal. In order to make the KHP crystal technologically important, we have prepared Crystals of the equimolar composition of Bismuth as Bismuth nitrate with KHP. The effect of doping is studied using Optical, Single crystal XRD, Powder XRD and SEM-EDS.

Experimental

Synthesis and Crystal Growth

Potassium hydrogen phthalate crystals (Qualigens) is purified by repeated recrystallization and the crystals are grown by a slow evaporation solution growth technique (SEST). A saturated KHP solution is prepared(12g/100ml) and Bismuth in the form of Bismuth nitrate is used as such. An equimolar composition of Potassium Hydrogen Phthalate and Bismuth nitrate (1:1) is prepared using triply distilled water as solvent. It was stirred for 3hrs , Filtered in the beaker and covered with polythene sheet provided with holes. The solution is maintained in ambient condition for 20 days, at 9th day seed Crystals were found and 17th day bulk crystal were found and are harvested. The 20th day bulk crystal which was clear in growth medium are images of as grown doped and undoped crystals are in the fig 1 (a),(b

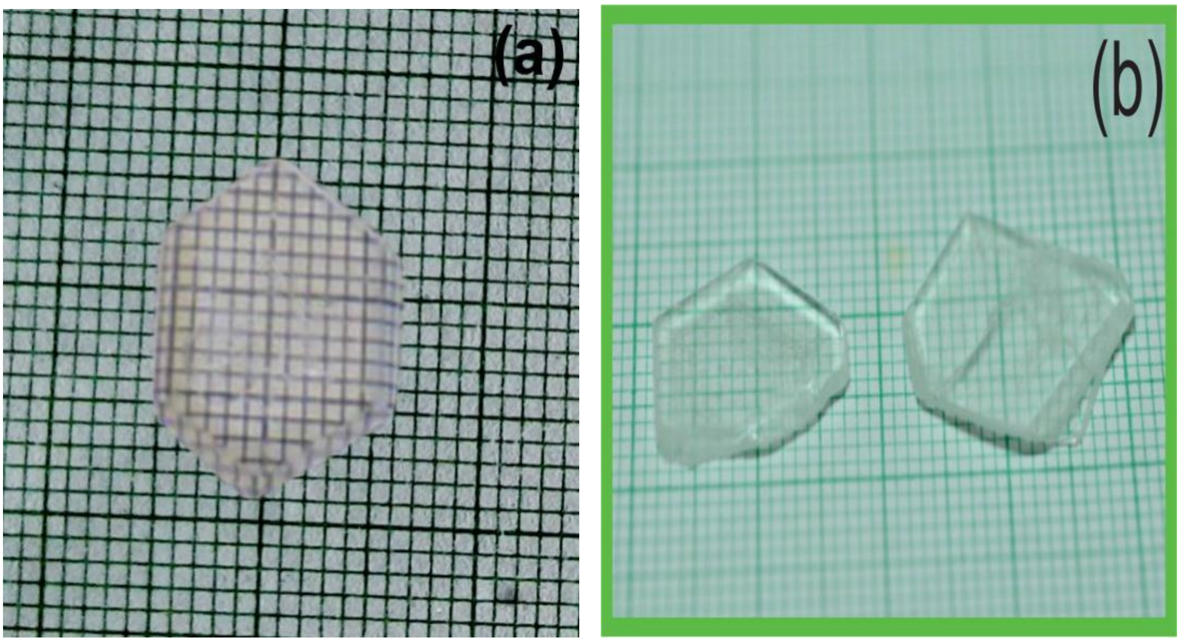

Fig.1 Images of (a) Pure KHP (b) Bi doped KHP crystal

Characterization Techniques

The surface morphology as seen through a JEOL JSM 5610 LV scanning electron microscope, which can magnify objects up to 2,000 times at a resolution of 3.0 nm with an acceleration voltage range of 0.3 to 30 kV.

A chemical microanalysis method called EDS is used in tandem with a scanning electron microscope. Bruker AXS (Kappa APEX II) X-ray diffractometer was used for single crystal x-ray diffraction research. Powder XRD can provide information about crystalline structure (or lack there of) in a sample even when the crystal size is too small for single crystal X-ray diffraction. Data were analysed with the PAN analytical X pert PRO X-ray diffractometer at room temperature using graphite mono chromated Cu Kα radiation (1.54060 A^0AVATAR 370 FTIR Spectrometer was used to record Fourier transform infrared spectra. UV-VIS spectra were recorded using spectrophotometer JASCO V530. TGDTA curves were recorded by using SDT Q600 (TA instrument) thermal analyzer. The second harmonic gerneration test on the crystal was performed by the Kurtz powder SHG method.

Results and Discussion

Scanning Electron Microscopy (Sem) With Energy Dispersive X-Ray Spectroscopy (Eds)

The influence of the dopant on the surface morphology of Potassium Hydrogen Phthalate faces reveals structure defect centers as shown in fig.2 Bi (II) Doped KHP in the growth medium, shows a fibrous structure. The pure one shows the highest surface roughness due to bunched steps or even macro steps than the doped one with lowest surface corrugation.

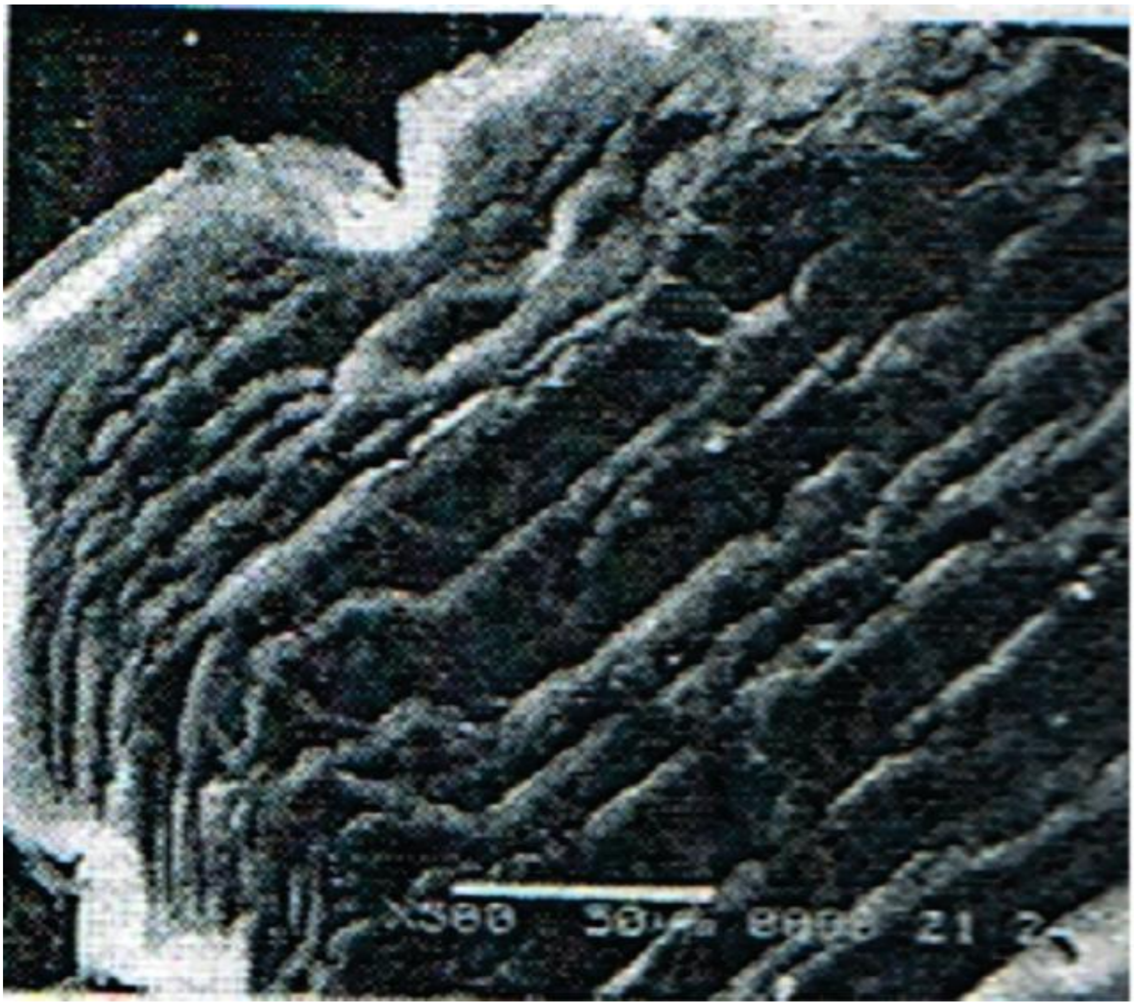

Fig .2 SEM incorporation (a) pure KHP

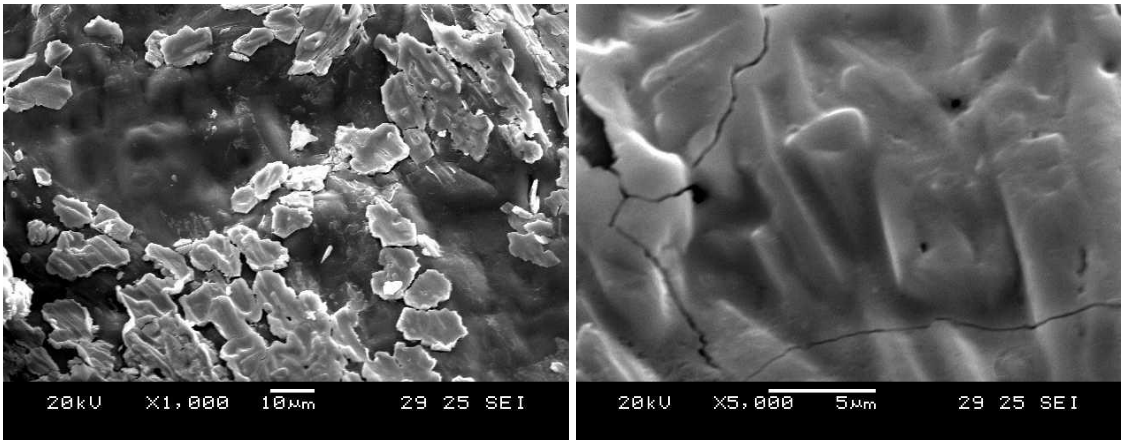

Fig.3 (b) Bismuth doped KHP Crystal

The EDS graph confirms the presence of Bi(II) in the crystalline matrix(fig-3) .Analysis of the surface at different sites show that only a small quantity of dopant has incorporated on KHP Crystalline matrix which is non uniform over the surface connected to adsorption mechanism. Fig 4

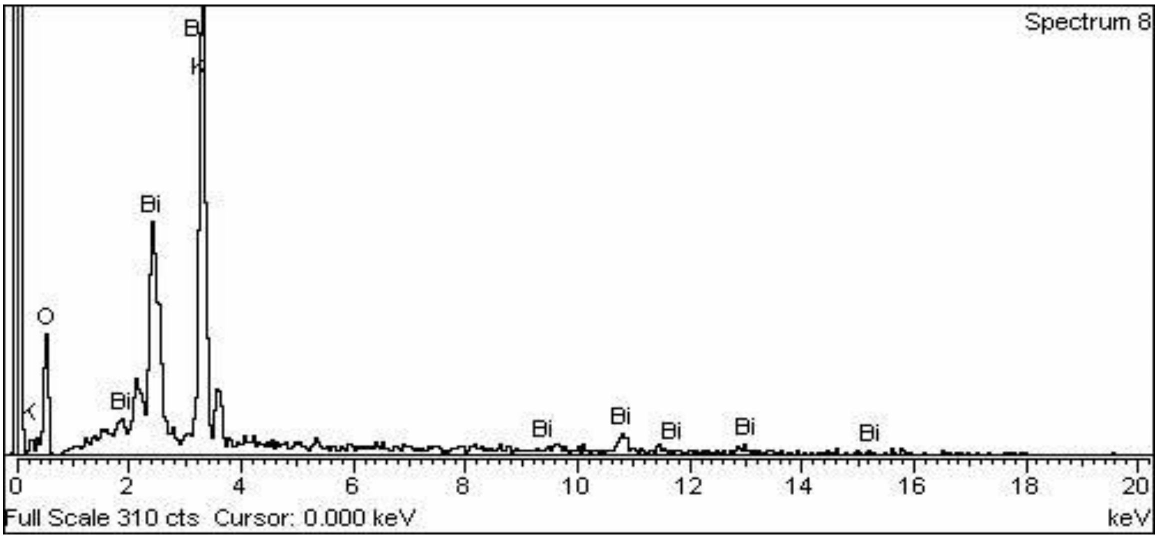

Fig.4 EDS graph of Bi doped KHP Crystal

Single Crystal XRD Analysis

The cell parameter values for Pure and Bismuth doped KHP crystals are shown in the table-1 The values of doped Crystal is reduced compared to pure one. From this single crystal XRD values we can say that the dopant can enter into KHP crystalline matrix and cause slight distortion in it. The cell parameters values are shown in the table -1

Table -1-cell parameter values of pure and Bi doped KHP crystal

Lattice Parameter	a A^0	b A^0	c A^0	V A^{03}	System
Values	9.6120	13.3290	6.4820	830.46	Orthorhombic
KHP	5.39	6.39	9.13	315A^0	Orthorhombic
KHP\Bi					

Powder XRD Analysis

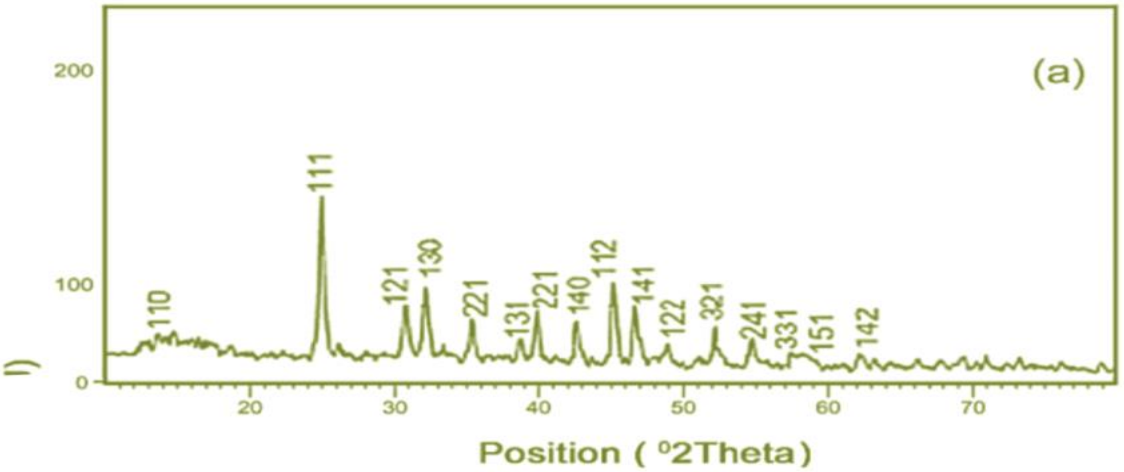

Fig 5 (a) Powder XRD graph of Pure KHP

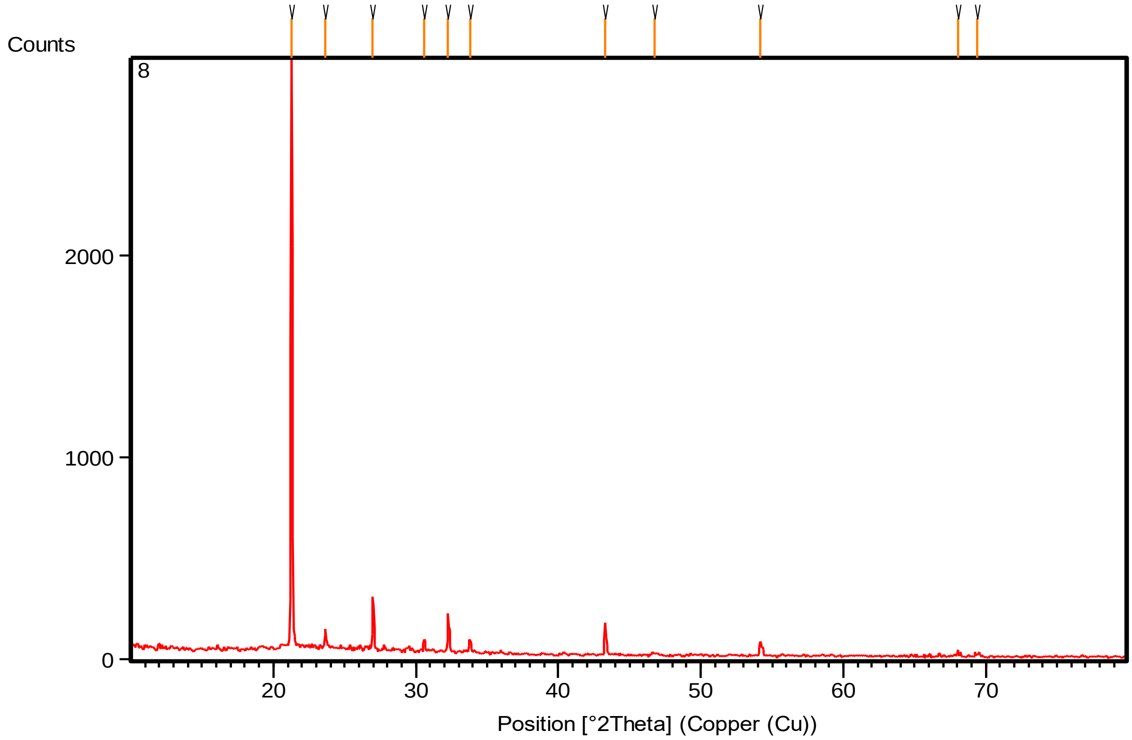

Fig. (b) Powder XRD graph Bi doped pure KHP

The powder XRD patterns of Pure and Bi (II) doped KHP are given in fig- 5a,b In this specimen the relative intensities of peaks are reduced compared to pure one which may be due to doping of Bismuth to KHP. The particle size is 16.37 nm which could be calculated using scherrer equation , **t= K λ/(β cosθ).**Where t- Average dimensions of crystallites. K is the Scherrer constant; λ is the wavelength of Xray ; θ peak position in radian and β integral breadth of reflection(in radian 2θ) located at 2θ.

Fourier Transform Infrared Spectroscopy (FTIR)

The characteristic vibrational frequencies of pure potassium hydrogen phthalate are shifted to higher vibrational frequencies due to doping with Bismuth (Fig.6 a, b). The shifting could be due to the lattice strain developed by the dopant to KHP crystal matrix. An absorption band in the region 500 to 900cm^{-1} could be due to C-H out of plane deformations of aromatic ring. Table 2 The symmetric and asymmetric stretching frequency of O-H-O appeared at 1199.72cm^{-1} , 1139.73cm^{-1} and 1068.56Cm-1 fig 6 a, b

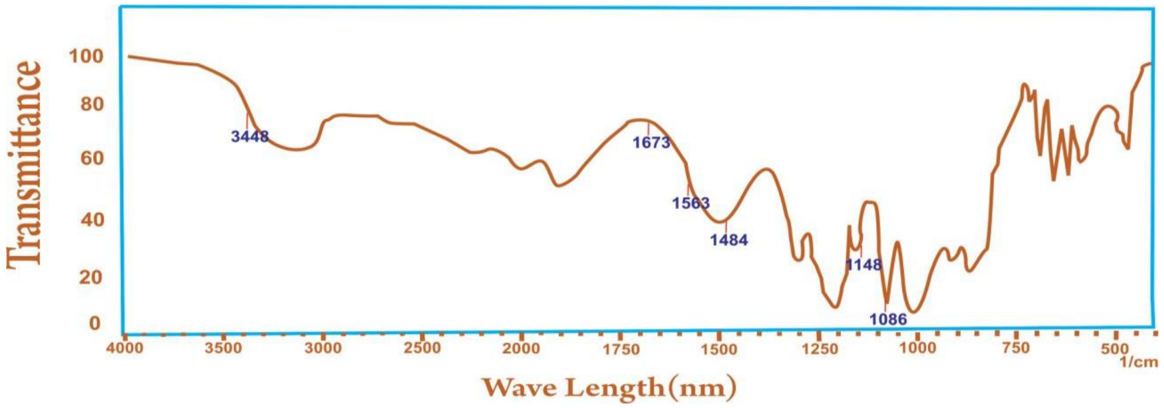

Fig.6 FTIR Spectra of (a) pure KHP

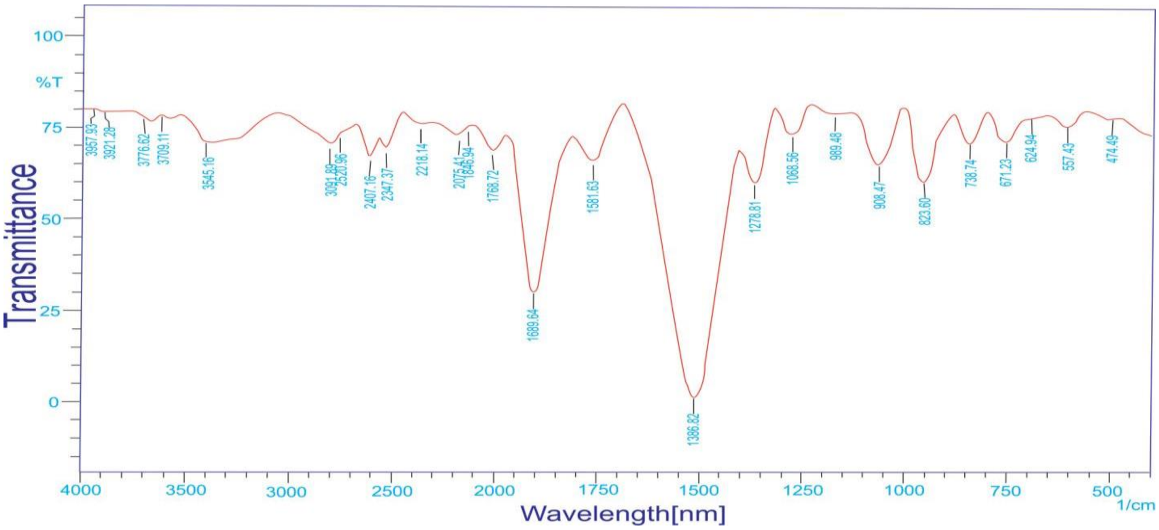

Fig.6 (b) Bismuth doped KHP Crystals

Table-2-Comparison of vibrational frequencies of pure and Bi doped KHP Crystal

S. No	**KHP**[a] **Cm-1**	**Bi/KHP** * **Cm-1**	**Assignment**
1	1563	1581.63	ν_sO-C = O
2	1484	1386.82	ν_{as} O-C = O
3	1086	1068.56	ν_{as} O-H-O
4	1148	1139.93	ν_s (O-H-O)
5	1673	1689.64	ν_s C = O
6	3448	3545.16	ν_s(OH)

a-ref.[18]. (*)Present work

UV-VIS-NIR Spectroscopy

The UV-visible absorption spectrum of pure and Bi (II) doped KHP are shown in (fig-4.5) Due to its high transmittance and absorption in the visible region, it is widely used for optical window application with lower cut off wavelength at 244 nm and 301nm revealing better NLO of the doped crystal then pure one. The band gap energy can be calculated by equation,

$$E\,g = h\,c / \lambda\ max$$

$$E\,g = 1.243 \times 10^3 / \lambda\ max$$

Where

h – Plank constant

c – Velocity of light

The band gap energies are calculated as 5.09 and 4.13 for doped one and 4.93 for pure KHP. So with higher band gap energy the sample can be applied for optical purposes. Fig 7 a, b

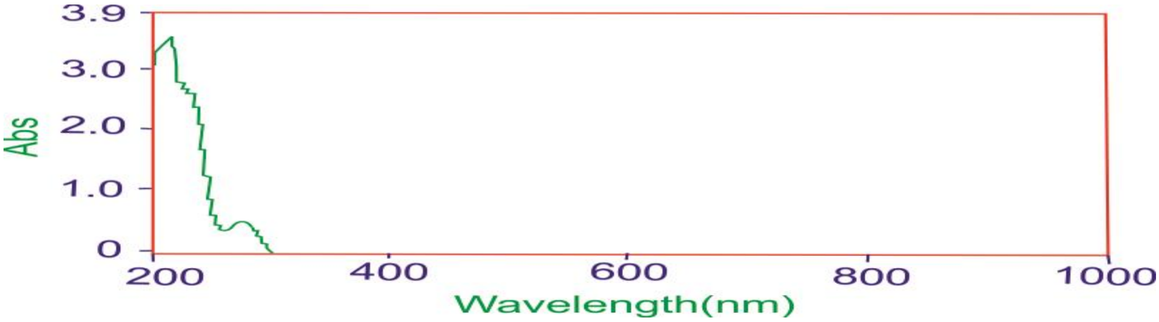

Fig.7 UV Spectra of (a) pure KHP

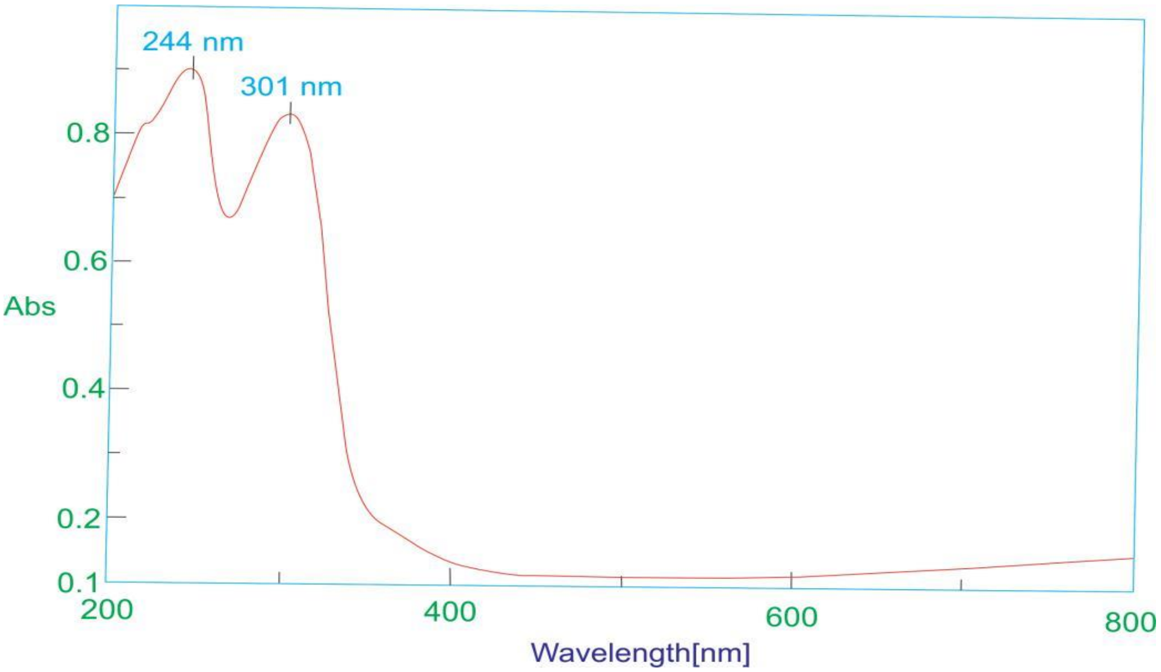

Fig. 7 (b) Bismuth doped KHP crystals

Thermal Studies

Fig 4.6 shows the TG-DTA curves of pure KHP and Bi (II) doped KHP crystals. The thermal analysis reveal that there is no physically observed water in the molecular structure of crystals growth from doped KHP solution studies reveal the purity of the material. The DTA curve of Bi doped KHP crystal endothermic peaks at about 180^0 c and 320^{0}c peak at about 170^{0}c which are broad. TG curves shows decomposition at around 200^{0}c with mass loss 40-70% compared to pure 300^0 c suggesting the sublimation of the material for application in lasers where the crystals are required to withstand high temperatures. Fig 8 and 9

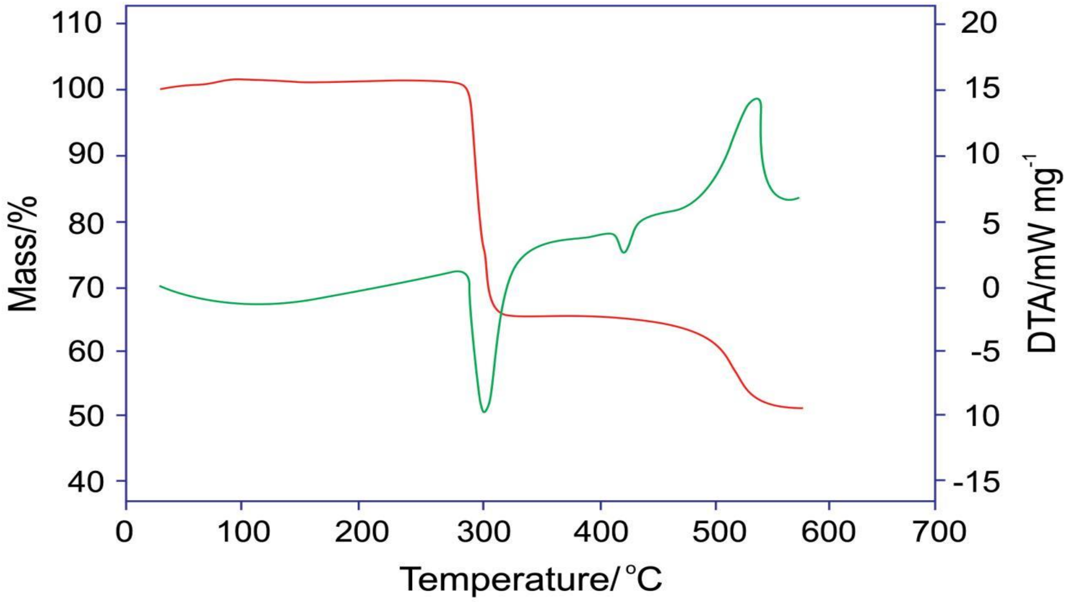

Fig.8 TGDTA graph of Pure KHP

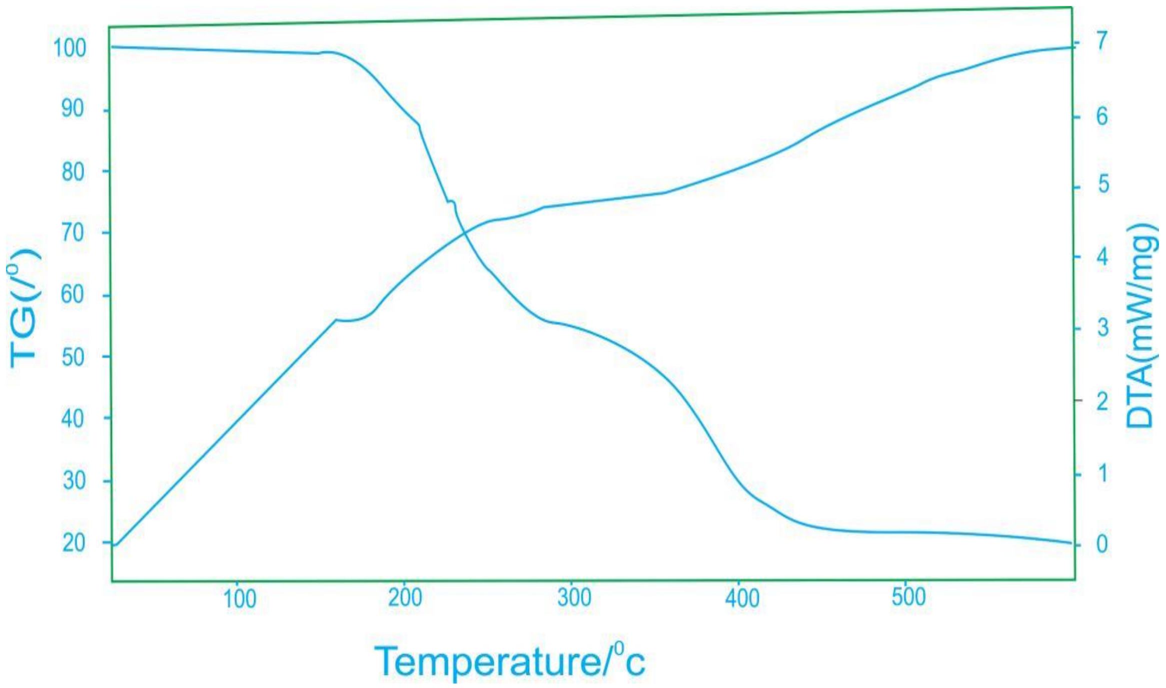

Fig.9 TGDTA graph of Bismuth doped KHP

SHG Efficiency

SHG test is performed on the powdered samples with the input radiation of 2.9mJ/pulse. The output SHG intensities (Table-3) for pure and doped specimens gives relative NLO efficiencies of the measured specimens. There is a significant enhancement in the SHG efficiency due to dopant. Latest report reveal that enhancement in crystalline perfection could lead to improvement in SHG efficiency [19].

SHG Output

Table-3 SHG Output

SYSTEM	**$I_{2\omega}$/V**
KHP	1.07
Bi/KHP	6.40

CONCLUSION

Highly transparent crystals of pure and Bismuth doped KHP crystals are grown By SEST method. We have used FT-IR, XRD, TG-DTA, and Single crystal XRD lattice parameter values to study the influence of heavy doping of 'p' block metal (Bi) on crystals. The cell parameter values of single Crystal XRD of doped and undoped specimens reveals some minor variations. SEM-EDS confirms the presence of bismuth in the crystalline matrix. FT-IR shares some minor changes in the vibrational peaks of doped specimen than pure. UV-Visible spectra of doped specimen shows better transmittance with high optical properties. TGDTA reveals that the doped specimen is temperature resistant and can be applied in laser.SHG confirms that the doped sample is highly NLO material.

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