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Growth and Characterization of Pure and Fe^{3+} Doped KHP Nonlinear Optical Single Crystals

P. Rajasekar[1], K. Thamizharasan[2]

[1]Research Scholar, Department of Physics, Bharathiyar University, Coimbatore, Tamilnadu, India

[2]Associate Professor, Department of Physics, Sir Theagaraya College, Chennai, Tamilnadu, India

Abstract: ***Pure and iron doped single crystals of Potassium Hydrogen Phthalate were grown successfully by slow evaporation method. The concentration of dopant in the mother solution was 1 mol% and 1.5 mol%. There is a drastic change in the morphology due to variation in doping rates which is also reflected in the X-ray diffraction data. The Fourier Transform infrared spectroscopy study confirms the incorporation of metal ions into Potassium Hydrogen Phthalate crystal. The thermal study indicates the dissociating nature of the crystal. The nonlinear optical property of the grown crystal has been confirmed by Kurtz-powder second harmonic generation test. The dopant of 1 mol% and 1.5 mol% shows higher second harmonic generation result than pure Potassium Hydrogen Phthalate.***

Keywords: Potassium Hydrogen Phthalate, Nonlinear optics, Doping, Single crystal, Characterization

1. Introduction

Second order nonlinear optical materials have recently attracted much attention because of their potential applications in emerging optoelectronic technologies [1, 2]. Materials with large second-order optical nonlinearities, short transparency cutoff wavelengths, and stable physico-thermal performance are needed to realize many of these applications. The search for new frequency conversion materials over the past decade has concentrated primarily on organics. It has been demonstrated that organic crystals can have very large nonlinear susceptibilities compared with inorganic crystals, but their use is impeded by low optical transparency, poor mechanical properties, low laser damage threshold, and the inability to produce and process large crystals [3, 4]. Purely inorganic nonlinear optical (NLO) materials typically have excellent mechanical and thermal properties with relatively modest optical nonlinearities because of the lack of extended π-electron delocalization. In semi-organics, polarizable organic molecules are stoichiometrically bound within an organic host [5].

In recent years, the NLO properties of semi-organic complex products have attracted great interest because these metal-organic complexes combine the high optical nonlinearity and chemical flexibility of organics with physical ruggedness of inorganics [6,7]. Transition metals Cu, and Ni has been employed as a dopant for many materials for many years. Metal ions doped nanoparticles can be utilized as a non-precious catalysts. The growth of semi-organic crystals in the presence of metal ions showed good transparency and mechanical strength. The saturation magnetization and remnant magnetization have been increased with increasing metal ion concentration. Therefore, doping enhances the thermal stability of the grown crystals and also significantly inhibits the growth of anatase crystal size.

Good quality of nonlinear optical (NLO) materials can be produced by modifying various structural and physical properties of crystals by introducing transition metal dopants. It is reported to induce significant changes in structural, thermal, linear and non-linear optical properties in KDP, ADP, KAP, BTZC crystals [8–12]. Therefore, the aim of the present work is to investigate the effect of pure and Iron (Fe^{3+}) doping on the growth and optical properties of KHP single crystals.

2. Experimental Procedure

2.1. Crystal growth

Pure KHP and doped crystals were grown by the slow evaporation technique under room temperature. Commercially available KHP salt (AR grade) was dissolved slowly in a double distilled water until a saturated solution was obtained. Ferric ions (Fe^{3+}) in the form of $FeCl_3$ at 1 and 1.5 mol% is used as dopant. In order to get a clear homogeneous solution, the saturated aqueous solutions of pure and Fe^{3+} doped KHP were stirred for about 10 hours. The solution was filtered with a microfilter and stored in the isolated beakers covered with perforated sheets. The seed crystals were permitted to float on the surface of the saturated solution and left for slow evaporation at room temperature. The crystallization took place within 25-30 days and the optically transparent crystals of metal ions doped KHP were attained with optimal size and shape. The photographs of both pure and doped Fe^{3+} crystals are given in Figure 1.

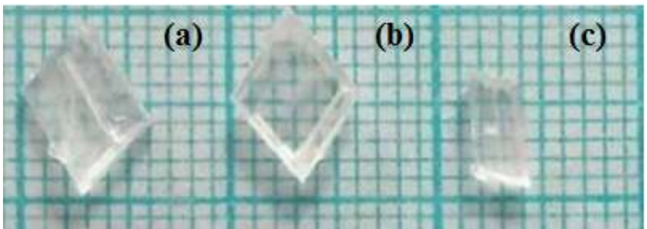

Figure 1: The photographs of (a) pure KHP, (b) 1 % Fe^{3+} doped crystals and 1.5 % Fe^{3+}doped crystals

2.2 Characterization

Various characterization techniques have been adopted to study the enhanced properties of grown crystals. The functional groups were observed using Perkin Elmer

Spectrum in the range of 500-4000 cm^{-1}. The crystal structure of the grown single crystals of pure and Fe^{3+} doped KHP were confirmed by powder X-ray diffraction using ENRAF NONIUS CAD-4 powder crystal X-ray diffractometer with CuKα radiation. The optical properties of the crystals were examined between 100 and 1000 nm using LAMBDA-35 UV-Vis spectrophotometer. Differential thermal and thermo gravimetric analysis has been carried out to study the thermal stability for the grown crystals using a simultaneous thermal analyzer TGA7 (Perkin Elmer). The instrument Matsuzawa MMT-X (Japan) was used to study the Vicker's hardness. Vickers hardness tester fitted with a Vickers diamond quadrangular pyramidal indenter. Loads ranging from"5, 10, 25, 50, 100 g" were used for making indentation with constant time of 5 s. The Kurtz and Perry method was performed to calibrate the SHG efficiency of all the grown crystals.

3. Results and Discussion

3.1 Structural analysis

X-ray diffraction (XRD) analysis was performed to identify the crystallinity and crystal phases of the grown crystals. The XRD data of pure crystal was compared with the JCPDS data (24-1870 & 31-1855). The lattice parameters a, b, c and unit cell volume (V) of the crystals were calculated from the following equations for the orthorhombic crystal system.

$$\lambda = 2d_{hkl}\sin\theta_{hkl}$$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

$$\text{and volume } V = abc$$

Where d is the lattice spacing, and (h, k, l) is the Miller indices, a, b and c are the lattice parameters, λ is the wavelength and 2θ is the diffraction angle. The obtained lattice parameter values are given in Table 1. It indicates that there is a slight change in lattice parameters of doped crystals and it is tabulated in Table1. The pure and doped crystals belong to orthorhombic structure.

Table 1: Lattice parameters of pure and Fe^{3+} metal ions doped KHP crystals

Crystal	Lattice parameters (A°)			Phase
	a	b	c	
KHP	9.612	13.591	6.381	Orthorhombic
1%Fe^{3+} KHP	9.527	13.489	6.301	Orthorhombic
1.5%Fe^{3+} KHP	9.512	13.564	6.357	Orthorhombic

3.2 Optical transmission spectral analysis

Optical transmission spectra were carried out for the pure and Fe^{3+} grown crystals in the wavelength region from 100 to 1000 nm. The spectrum is shown in Fig. 2. The Fe^{3+} (1.5 %) doped KHP crystals reveal higher transmittance compared to the pure and 1% Fe^{3+} doped KHP crystal. The cut off wavelength is nearly 300 nm for all the grown crystals. It is found that both pure and metal ions doped KHP crystals have good transmission in the visible region. Since the transmission window is observed in the visible region, the grown crystals could be suitable candidate for optoelectronic applications [13-14]. The results indicate that an increase of Fe^{3+} concentration enhance the transmittance in visible region.

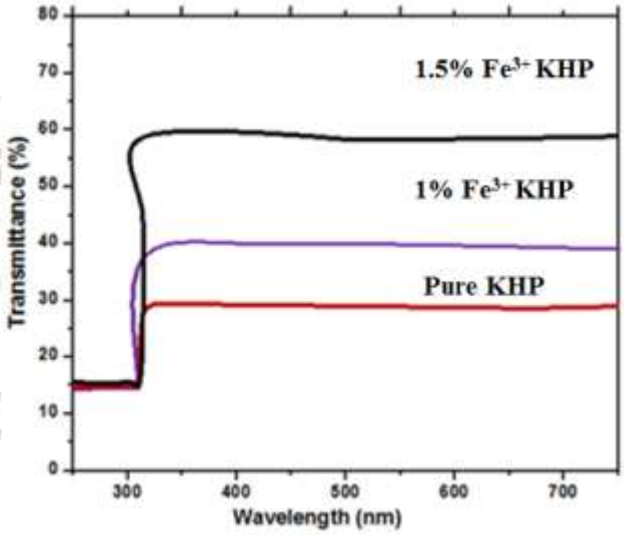

Figure 2: UV–Vis spectra of pure and Fe^{3+} ions doped KHP crystals

3.3 FT-IR analysis

The FT-IR spectrum were performed for the pure and Fe^{3+} doped crystals. The pure KHP crystal is displayed in Figure 3. The OH symmetric stretching is observed at 3788, 3415 and 3008 cm^{-1}. Strong band around 2822, 1586, 1514, and 1290 cm^{-1} in the spectra associates to the combination band of stretching. Vibrations exist at 1858, 1647, and 1458 cm^{-1} attributed to the OH plane bending. Further, strong band at 605 cm^{-1} can be corresponded to CH in plane bending. Vibrational assignments of pure and Fe^{3+} ions doped KHP crystals are tabulated in Table 2.

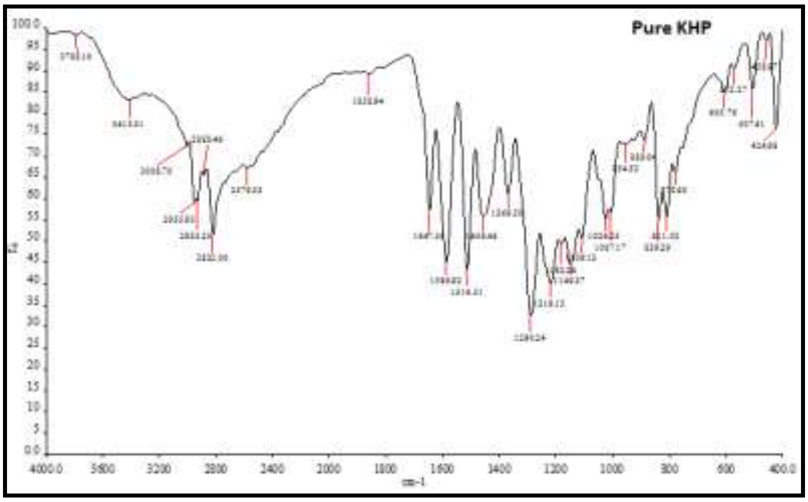

Figure 3: FTIR spectra of pure KHP crystal

The detected frequencies are found to be in good agreement with the reported values [15]. The XRD and FTIR results confirm that the doped crystal preserves its original structure.

Table 2: Vibrational assignments of pure and Fe^{3+} ions doped KHP crystals

KHP	1 % Fe^{3+} KHP	1.5 % Fe^{3+} KHP	Assignment
3788	3792	3791	O-H symmetric stretching
1290	1295	1298	C-H aromatic stretching
1369	1440	1442	C-H out of plane bending
1586	1590	1588	C-C stretching
1026	1030	1032	O-H in plane bending
605	612	608	C-H in plane bending
424	428	432	O-H out of plane bending

3.4 Thermal analysis

Thermo gravimetric and differential thermal analysis was performed in the temperature range between 100 °C to 600 °C under the nitrogen atmosphere. TG and DTA curve for pure and Fe^{3+}metal ions doped KHP crystal is given in Figure 4. No weight loss is found up to 240 °C for pure and doped KHP crystals. The decomposition starts around at 250 °C for all the grown crystals.

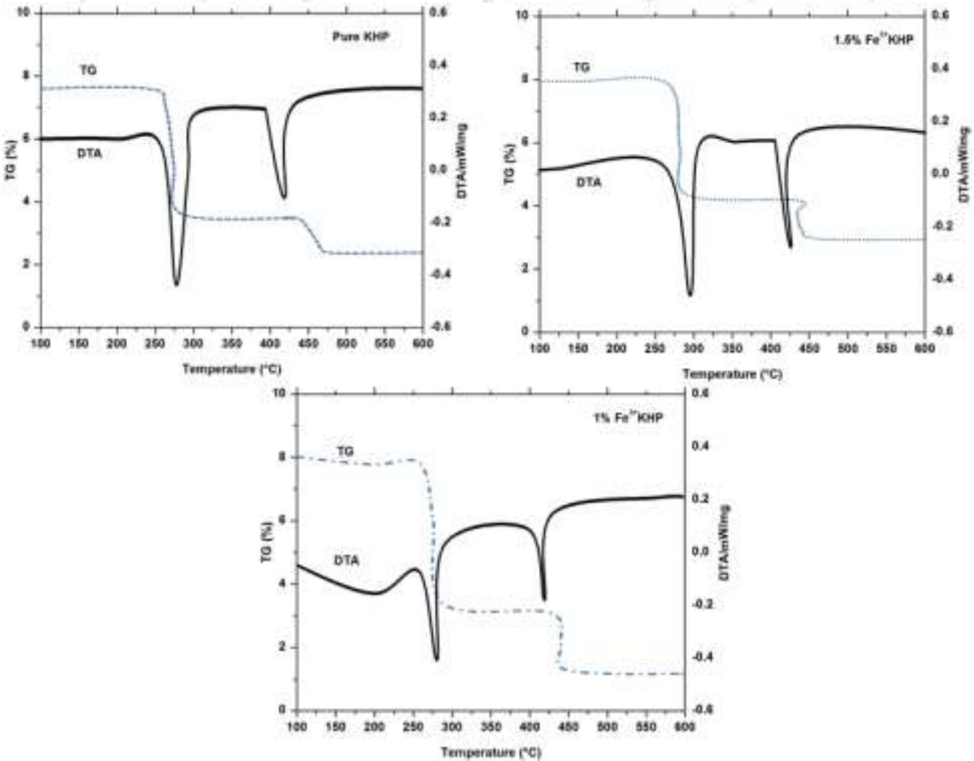

Figure 4: TG/DTA curves of the grown pure and Fe^{3+} metal ions doped KHP crystals

The peak of endothermic curve is observed at 275, 288 and 296 °C. These peaks are associated to the pure, 1% Fe^{3+} doped KHP, 1.5% Fe^{3+} doped KHP crystal respectively. As a result, grown crystals have good thermal stability and can be used for the practical applications.

3.5 Microhardness studies

The Leitz Wetzler Microhardness tester with a diamond pyramidal indenter has been carried out to study the mechanical stability [16]. This experiment has run for the various loads from 25 to 100g in the steps of 25g with a constant indentation period of 25s for all loads. Vicker's hardness number (H_v) is measured using the relation

$$H_v \frac{1.8544\,P}{d^2} kg/mm^2$$

Where 'P' is applied load in kg and 'd' the diagonal length in mm. The variation of H_v with applied load P is shown in Fig. 5. From the Figure 5, it was observed that hardness is increased with increase of load and mechanical strength is enhanced for the doped KHP crystals than pure. This may be due to strong bond formation of Fe^{3+} ions with the phthalate group. The improvement of hardness by dopant increases the possibilities of these crystals towards optical device applications.

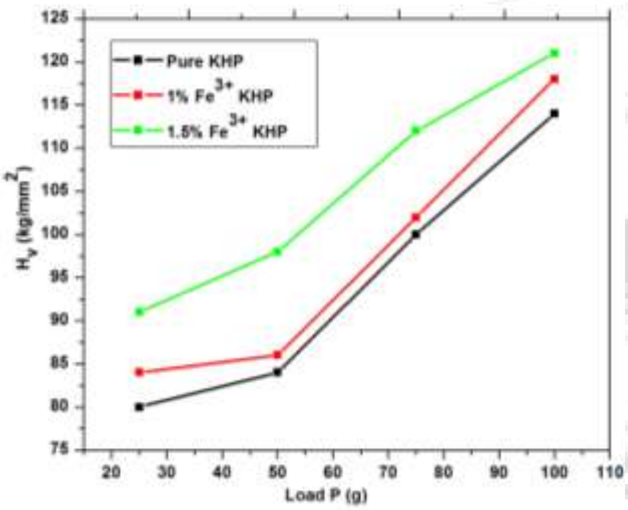

Figure 5 The variation of H_v with applied load (P)

3.6 The SHG efficiencies

The SHG efficiencies were estimated for the doped crystals with reference to that of pure KHP. The SHG efficiency for pure and doped crystals is given in Table 3. Results denote that doping metal ions lead to significant enhancement in the SHG efficiency of KHP crystal due to catalytic effect on the NLO properties. Enhancement of SHG efficiency is attributed to molecular alignment, it increasers the nonlinearity.

Table 3: Values of SHG efficiency for pure and metal ions doped KHP crystals.

Crystal	SHG Output (mV)
Pure KHP	21
1 mol % Fe^{3+} KHP	36
1.5 mol % Fe^{3+} KHP	48

4. Conclusion

Pure and Fe^{3+} doped KHP crystals were grown from the aqueous solution using slow evaporation technique. Powder XRD results confirmed the material of the grown crystals are orthorhombic structure in nature. The FTIR analysis revealed the existence of functional group of grown crystals. The TG/DTA analysis shows that the thermal stability was not affected by the dopant. The higher SHG efficiency was observed for the doped crystals which can enhance the NLO properties.

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