Research Article **CODEN: IJRPJK** **ISSN: 2319 – 9563**

IJRPNS

International Journal of Research in Pharmaceutical and Nano Sciences

Journal homepage: www.ijrpns.com

GROWTH AND CHARACTERIZATION OF METHYL ORANGE DOPED KAP CRYSTALS - A POTENTIAL MATERIAL FOR OPTICAL AND SECOND HARMONIC GENERATION APPLICATIONS

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ABSTRACT

Undoped and methyl orange doped KAP crystals were grown by slow evaporation solution growth technique. The grown crystals were subjected to single crystal and powder x-ray diffraction analysis in order to estimate the structural parameters. The presence of functional groups and the spectral properties were assessed by FTIR analysis. The optical properties were examined by UV-Visible spectral analysis. The thermal stability and the mechanical stability were evaluated by TG/DTA and Vicker's micro hardness test respectively. NLO studies provide information regarding the SHG efficiency of the specimens and the results suggest that methyl orange doped KAP crystals are potential candidates for NLO device applications.

KEYWORDS

Semiorganic, Optical Materials, FTIR, NLO and XRD.

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INTRODUCTION

Potassium acid Phthalate (KAP) is a well-known semi organic NLO material possessing platelet morphology[1]. The cleavage faces favours the use of KAP crystals as substrates in epitaxial thin film technology and these films were observed to have high nonlinear susceptibility[2]. KAP crystals have well developed surface pattern on the (010) plane, that can be easily observed by means of an optical microscope[3-5]. KAP belongs to alkali acid phthalate family that crystallizes in orthorhombic symmetry with a space group of $Pca2_1$[6]. Potassium acid phthalate crystals are easily grown by slow evaporation solution growth technique with water as a solvent and it has 14 natural growth faces with dominating (010) face. The (010) face is more suitable for any surface morphological studies[7]. Tune able solid state lasing materials are researched extensively and exploited for the growth of polymers, clays or liquid crystals. An easily growing NLO single crystal combines the quality of liquid dye lasers. The properties such as high efficiency and broad band tuneability with the flexibility and the convenience operation offered by the solid state lasing media are taken into consideration while the design of NLO materials[8]. Hence dyes were also used as dopants for enhancing the optical characteristics of crystals. A review report presents the significance of Dye Inclusion Crystals (DICs). The report also highlights the emergence, disappearance, and restoration in the laboratory conditions of DICs. The report includes the recent contributions on dyed sulfates, chromates, phosphates, carboxylates and carboxylic acids, carbonates, nitrates, halates, halides, amines, amides, and sugars. The work also reports how dyed crystals address issues of interest to contemporary crystallographers, materials scientists, and spectroscopists as well as physical, organic, analytical, biostructural, and stereochemists[9]. The dye molecule is incorporated with the water soluble crystals and avoids many drawbacks like other solid materials such as working media for lasers[10]. The dyes absorb light in the visible region and thus second harmonic generation of Nd: YAG laser light is suitable for pumping the dyes in order to achieve lasing effect[11]. Due to broad absorption in the visible region of dye doped crystal it can be used as a filter. Several other crystals such as potassium nickel sulphatehexahydrate and cesium nickel sulphatehexahydrate are reported being used as filters[12,13]. An easily growing nonlinear optical (NLO) single-crystalline material that combines the qualities of liquid dye-lasers such as high efficiency and broad band tuneability with the flexibility and the convenience in operation offered by a single crystal is a very interesting alternative. Such an alternative may be represented by dye doped single crystals of KAP[14]. The lowest concentration of some organic impurities, such as Chicago sky blue, amaranth and sunset yellow could slightly distort the KDP lattice and thereby introduce local deformations, which are assumed to be the original reason that causes the changes of optical properties[15-18]. The up conversion luminescence in dye doped KAP crystals was reported by J.B. Benedict *et al*[19]. Following the work stunning tricoloured crystals with three distinct regions of green, yellow and orange luminescence were deposited in the solutions of KAP that contained a dye “Proflavin”[20]. It was reported that the dye serves as a fluorescent probe of surface charge while identifying the polar crystallographic axis. Growth of Coumarin doped KAP crystals by Monica Enculescu reports that Coumarin 6 (C6) is an important laser dye in the blue- green spectral region and is widely used in dye lasers[21]. Eric D Bott[22] used dichloroflurocein (DCF) dye as a dopant so as to study the dispersion kinetics in KAP crystals. The results demonstrate that two populations exist in KAP one demonstrates single exponential excited state decay over the course of the blinking trace and the other explains stretched exponential decay. M. Enculescuet. al, reported the influence of Rhoda mine 6G on the optical properties of KAP crystals and it was observed that the intensity of the absorption bands increase with dye concentration for KAP crystals[23]. Based on these reports, a dye namely methyl orange was used as an additive in the present investigation. It was observed that methyl orange dye enhances the optical, thermal and mechanical properties which are discussed in detail. From the results it is inferred that dye doped KAP crystals are efficient materials in optical filter and NLO applications.

Experimental details

Materials used

Analytical reagent grade Potassium acid Phthalate (commercially known as potassium hydrogen phthalate, Merck) and Methyl Orange (Merck) were used as starting materials. The precursors were used without any further purification process since the purity of the starting materials was 99.5%. Deionised water (Merck) was used as the solvent.

Synthesis and Growth of Undoped KAP crystals and Methyl Orange doped KAP crystals

Calculated quantity of Potassium acid phthalate was dissolved in 100 ml deionised water and the solution was stirred using a magnetic stirrer at room temperature. A clear solution was obtained after 4 hours of stirring. The solution was filtered using a Whatman filter paper and kept covered in a place which is free from dust and external disturbances. Undoped KAP crystals were obtained after a time span of 27 days. Methyl orange dye was added to the Undoped KAP solution in the molar ratio of 0.1% by weight and stirred for 5 hours at room temperature. The clear solution was filtered using a Whatman filter paper and was kept in a dust and vibration free zone. Growth of methyl orange doped KAP crystals were observed after a span of 32 days. The photograph of the grown methyl orange doped KAP crystal is shown in Figure No.1.

Single crystal XRD

Single crystal XRD is a non-destructive technique which provides detailed information about the internal lattice of the crystalline substances including unit cell dimension. The grown crystals are subjected to single crystal XRD studies using an ENRAF NONIOUS CAD4 X-Ray diffract to meter equipped with a MoKα radiation (λ=0.71073 Å) to determine the unit cell parameters. Undoped and dye doped KAP crystals were found to crystallize in orthorhombic symmetry with the space group of $Pca2_1$. The cell parameters for Undoped KAP is a= 6.56 Å, b=9.60 Å, c=13.31 Å α=β=γ=90° and the volume of the unit cell was found to be 838.21 $Å^3$. The unit cell parameters of dye doped KAP was found to be a=6.45 Å, b= 9.57 Å, c=13.27 Å α=β=γ=90° and the volume of the unit cell was found to be 819 $Å^3$. The observed results are in good agreement with the reported literature[24]. The obtained results show that the inclusion of dye doesn't alter the structure of KAP crystals instead it alters the lattice parameters slightly. Hence slight variations in the lattice parameters viz., decrease in the unit cell values and volume without a change in the crystal structure confirms the addition of dopant successfully into the crystal lattice of the parent material.

Powder X-Ray Diffraction analysis

The powder XRD pattern was obtained by subjecting the powdered samples to JEOL JDX-8030 Powder X- Ray diffract to meter equipped with CuKα radiation with the wavelength of 1.503 Å. The pattern was obtained within the 2θ range of 10° to 90°. The material obeys the Bragg's condition for diffraction resulting in the formation of the powder XRD pattern. The powder XRD pattern of Undoped and dye doped KAP crystal is shown in the Figure No.2a and 2b. The prominent peak at the specific 2θ angle reveals the crystalline nature of the samples and the title material is in single phase. The sharpened peaks at the specific 2θ angles with good intensity were indexed by JCPDS software (card number PDF 31-1855). The sharpness of the peaks obtained indicates that the subjected samples were highly crystalline. The obtained pattern (Figure No.2a for KAP and Figure No.2b for MO-KAP) coincides well with the reported literature[17]. The change in lattice parameter values due to addition of dopants are responsible for the shifting of prominent peaks. Unit cell values for dye doped KAP were calculated from the powder x-ray diffraction data and the values are a=6.47 Å, b= 9.60 Å, c=13.29 Å. The volume of the unit cell obtained from the powder xrd pattern is V=825. 46 $Å^3$.

Fourier Transform Infrared spectroscopy

The Fourier transform infrared spectroscopy was effectively used to identify the functional groups of the samples. The crystals were finely powdered and mixed with potassium bromide. The mixture was made into pellets using a pelletizer and placed on the sample holder. The specimen was scanned within the wave number range of 400 cm^{-1} to 4000 cm^{-1} using a PERKIN ELMER RXI FTIR spectrophotometer in order to reveal the complex coordination. The Fourier Transform Infrared spectrum is shown in Figure No.3 (a) evidently shows that for Undoped KAP crystals, the absorption peaks observed around 2780 cm^{-1} and 2620 cm^{-1} corresponds to the O-H stretching vibration of the carboxylic acid whereas in the case of MO doped KAP crystals, these peaks gets shifted towards the lower frequencies and the absorption peaks are observed around 2779 cm^{-1} and 2617 cm^{-1} showing a red shift in the values. The absorption peak around 1381 cm^{-1} corresponds to the -C=O carboxylates ion symmetric stretching of =O. In the case of a dopant the absorption values show a red shift by shifting the peak to 1380 cm^{-1}. A marked decrease in the carboxylates ion and the carboxylic acid stretching was observed in methyl orange added KAP when compared to Undoped KAP which is due to the effect of dopant. Carboxylic stretching vibration is known to produce resolved multiple bands between 2500 cm^{-1} and 3400 cm^{-1}. The difference in sharpness of multiple bands may be taken as an evidence for the doping of methyl orange. In Undoped KAP, the absorption peak obtained at 1562 cm^{-1} corresponds to the asymmetric stretch of carboxylate ion. The asymmetric and the symmetric stretching vibrations occur in the bond between C and O which is seen as C=O. C-O symmetric stretching vibrations occur in absorption peak at 1282 cm^{-1}. The other stretching vibration occurs in the Undoped KAP spectrum is 1089 cm^{-1} and it corresponds to C-C-O stretching. Apart from this some bending vibrations and a wagging vibration occur due to the presence of the carboxylate group. The wagging vibration occurs at 681 cm^{-1} and it corresponds to the C-O wagging. The vibrations occurring at the 850 cm^{-1} and 441 cm^{-1} absorption peaks is attributed to the C-H out of plane bending and C=C plane bending respectively. One C=C-C out of plane ring deformation vibration occurs at the 549 cm^{-1}.

In the case of dopant the same peaks were observed with some slight shifts in the Undoped spectrum. Keeping the specifications of the equipment constant the same steps were followed by mounting the powdered dye doped KAP in the sample holder and the following absorption peaks were obtained. The absorption band appeared at 1562 cm^{-1} has been shifted to 1565 cm^{-1} which corresponds to the asymmetric stretching of carboxylate ion. The absorption peak that appeared at 1282 cm^{-1} for Undoped KAP now appears at 1262 cm^{-1} for dye doped KAP and it is attributed to the stretching vibrations of C-O. The shifted peaks at 1088 cm^{-1} is assigned to the C-C-O stretching vibration. The C-H out of plane bending and the C-C plane bending vibration is observed at 849 cm^{-1} and at 440 cm^{-1} respectively. A wagging vibration was observed at 682 cm^{-1}. The absorption peak at 548 cm^{-1} is assigned to the C=C-C out of plane ring deformation. Here the shifting of peaks denotes that the dopant is added into the crystal lattice of the KAP crystals successfully[20].

UV-Visible spectral analysis

Optical characterization is one of the significant tests done in order to evaluate the optical character of the sample. The optical properties such as the lower cut off, percentage of transmission and behaviour of the sample in the visible light region were examined by subjecting the samples to UV-Visible spectroscopy analysis. The analysis was carried out using a PERKIN ELMER LAMBDA 35 UV- visible spectrophotometer within the wavelength range of 190 nm to 1100 nm.

The traced UV spectrum is shown in Figure No.4 (a). From the UV spectrum it was observed that both Undoped and Methyl orange doped KAP crystals have a lower cut off wavelength at 290 nm. The addition of dopant does not alter the cut off wave lengths. Both the Undoped and doped samples possess the wide transparency window. The obtained percentages of transmission for Undoped and doped KAP crystals are 45 % and 58 % respectively. A sharp absorption was observed around 370 nm in the doped KAP crystals. The absorption of wavelength in the visible light region is the reason for the formation of colour in the crystal and owing to this property the dye doped material can be used as an optical filter for absorbing that particular wavelength. Also the lower cut off wavelength falls within the range of 300 nm and this makes the material a potential candidate in optoelectronic device fabrications. Hence it is inferred that dye doped KAP can serve as a better alternate for Undoped KAP in NLO devices that consist of KAP crystal as a prime material[16].

Estimation of Optical Constants

Optical constants such as the optical band gap, extinction coefficient and refractive index were estimated in order to know the optical property of the title materials. The optical band gap, (Eg) of Undoped and dye doped KAP crystals was estimated from the relation

$$h\alpha\nu = A(h\nu - Eg)^{1/2}$$

Where

A is the constant, h is the planck's constant, ν is the frequency of the incident photons

α is the extinction coefficient which is obtained from the transmisstance value

$$\alpha = \frac{2.3026 \log(\frac{1}{T})}{t}$$

The optical band gap was obtained by extrapolating the linear part of the plot between hν vs $(\alpha h\nu)^2$ which is shown in Figure No.4 (b). The optical band gap of Undoped KAP was estimated at 2.5 eV and that of methyl orange doped KAP is 2.8 eV.

Extinction coefficient (K) can be obtained from the relation $K= \frac{\alpha\lambda}{4\pi}$

The plot of extinction coefficient as a function of photon energy is shown in Figure No.4(c). An inverse dependence with E is observed in low energy value and a linear variation is observed with energy with addition.

The reflectance (R) and refractive index (n) can be derived from the relations,

$$R = \frac{1 \pm \sqrt{(1-\exp(-\alpha t) + \exp(\alpha t))}}{(1+\exp(-\alpha t))}$$

$$n = \frac{-(R+1) \pm \sqrt{(-3R^2 + 10R - 3)}}{2(R-1)}$$

The reflectance was also plotted as a function of photon energy and shown in Figure No.4 (d).

The refractive index was calculated from the plot of wavelength vs. refractive index and is shown in Figure No.4 (e).

The refractive indices for Undoped and dye doped KAP crystals are calculated and found to be 1.62 and 1.58 respectively. Dye doped KAP crystals possesses lower refractive index than the Undoped KAP crystals which is the most preferable property for antireflection coating in thermal instruments[25].

Thermal analysis

Before using a crystal for device fabrication it is very important to check the thermal stability of the grown crystal from various application points of view. The thermal expansion, specific heat and thermal conductivity are the main properties for lasers and high power systems therefore many researcher and scientists tried to grow the single crystal of various materials with high thermal stability and still searching good one. Hence TG/DTA analysis was carried out to check the thermal stability of the Undoped and Methyl Orange doped KAP crystals. The analysis was carried out in a closed chamber with controlled nitrogen flow atmosphere. The analysis was carried out up to the temperature of 1000°C at a heating rate of 20°C/min using a PERKIN ELMER THERMAL ANALYZER STA 409 PC in a nitrogen atmosphere. From the TG/DTA thermo gram it was found that the doped samples possess a better thermal stability than the undoped sample. The TG and DTA thermo gram of dye doped KAP crystals are shown in Figure No.5. From the TGA thermo gram it could be observed that there is no appreciable weight loss in both Undoped and dye doped KAP crystals around 100°C. This confirms that there is no water absorbed in the crystal. The onset temperature of the decomposition was found to be 240°C for Undoped KAP and 242°C for methyl orange crystals respectively. A research work done by Newkirk *et al*[26] and Belcher *et al*[27] on thermal behaviour of KAP in Nitrogen and air atmospheres reports that the KAP decomposes into K_2CO_3 and char at 800°C in Nitrogen atmosphere. The results obtained for pure KAP in the present work agree well with these reported results. From the DTA curve it is inferred that the sharp peak at 290°C and 301°C for Undoped and Methyl Orange doped KAP crystals corresponds to the melting point of the sample. It can be noted that the undoped sample has less melting point than the dye doped KAP crystal. The absence of other peaks before the melting point of the samples confirms that there is no other transition taking place in the material and this insures the thermal stability of the material for possible applications in lasers.

Microhardness of a crystal is defined as its capacity to resist indentation. In other words it can be described as the hardness of a material is a measure of its resistance to local deformation. It can also be correlated with other mechanical properties like elastic constants and yield stress of materials. Vicker's micro hardness test is one of the widely used analytical techniques to characterize crystals. The Mechanical property of the grown crystal was studied using LEITZ micro hardness tester, fitted with a Vicker's diamond pyramidal indenter. The indentation time was set as 5s for all the loads. The mechanical behaviour of the Undoped and dye doped KAP single crystals were analysed at room temperature. The selected surface (0 1 0) of the grown crystals were lapped, polished, washed and dried. Hardness measurements were taken for the applied load varying from 25 to 100 gm keeping the indentation constant at 10 s for all the cases. The Vicker's hardness number of the grown crystals was calculated from the relation $H_v = (1.8544 \text{ x } P)/d^2$ kg/mm^2.

Where H_v is the Vicker's hardness number in kg/mm^2, P is the applied load in kg, d is the average diagonal length of the indentation mark in mm. A graph was plotted between the Vicker's hardness number (H_v) and applied load P (Figure No.6). From the graph it was found that both the Undoped and doped KAP crystals are stable up to 100g. For loads above 100 g crack started developing around the indentation mark which is due to the release of internal stresses. The presence of cracks confirms the decrease in microhardness[13]. From the graph it is observed that the dye added KAP crystals are highly stable towards the application of mechanical stresses.

The observed changes in the micro hardness values of the dye doped KAP crystals is due to the strong interaction of O-H groups of KAP with the functional group of methyl orange. The strength of the crystal is computed from the log P-log d plot (Figure No.7) which yields a straight line and from its slope the work hardening coeffcient, n which is 2.6 for undoped KAP and 2.8 for methyl orange doped KAP. From the graph it can be found that undoped and dye doped KAP crystals come under the soft material category.

NLO test

Kurtz and Perry experimental set up remains to be a valuable tool for analysing the Second Harmonic Generation of materials. Powder SHG measurement was carried out using an Nd: YAG laser of 1064 nm wave length. NLO test was performed by Kurtz and Perry[28] experimental setup for NLO testing. The selected crystals were finely powdered and filled in a micro capillary tube. After sealing the capillary tube, the sample was subjected to Nd: YAG laser radiation and the SHG efficiency of the material was confirmed by a green emission of radiation. The reference material used was Potassium dihydrogen phosphate crystal. The input energy used was 3.2 mJ/pulse with a pulse width of 8 ns. The frequency conversion process was detected by a photomultiplier tube. The estimated SHG efficiencies of Undoped and methyl orange doped KAP crystals are 28 and 33 mV respectively. The SHG efficiency of Undoped KAP crystals is found to be 1.5 times and that of dye doped KAP crystals are found to be 1.8 times that of KDP crystal. Hence dye doped KAP crystals are found to be a better candidate for device fabrication in NLO technologies than pure KAP.

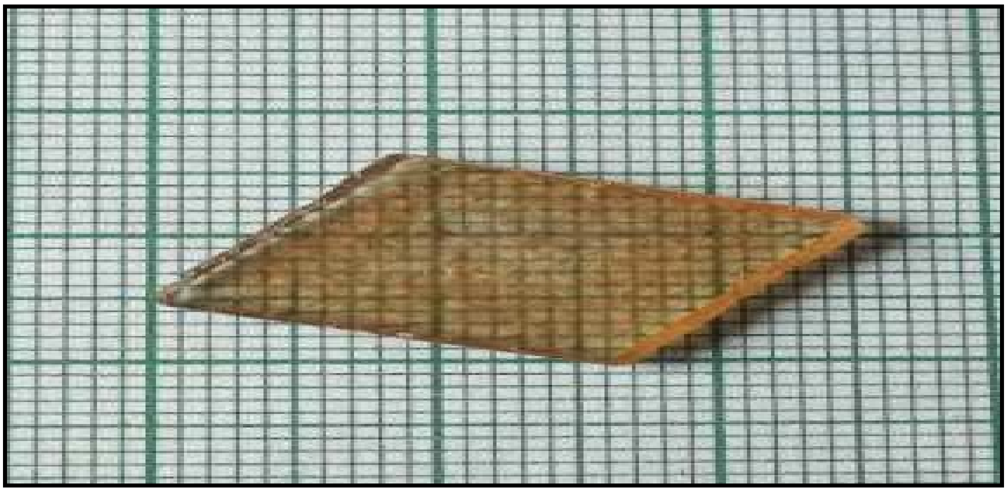

Figure No.1: As grown Methyl Orange doped KAP crystal

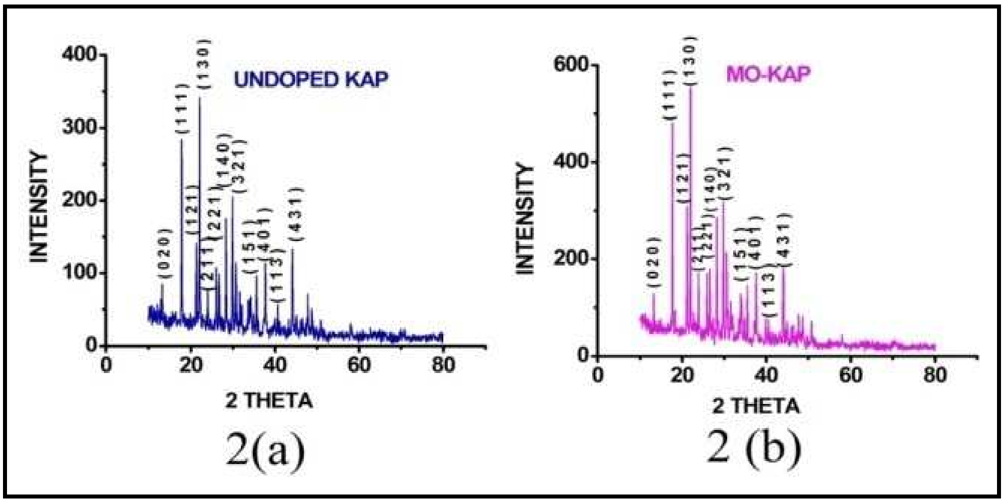

Figure No.2: Powder XRD pattern of (a) Undoped KAP (b) MO-KAP

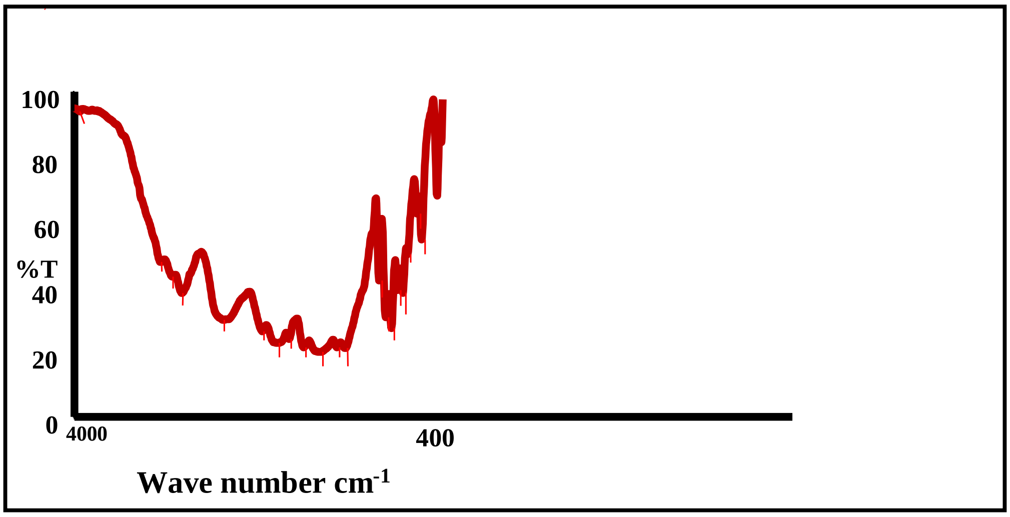

Figure No.3: (A) FTIR spectrum of Methyl Orange added KAP crystals

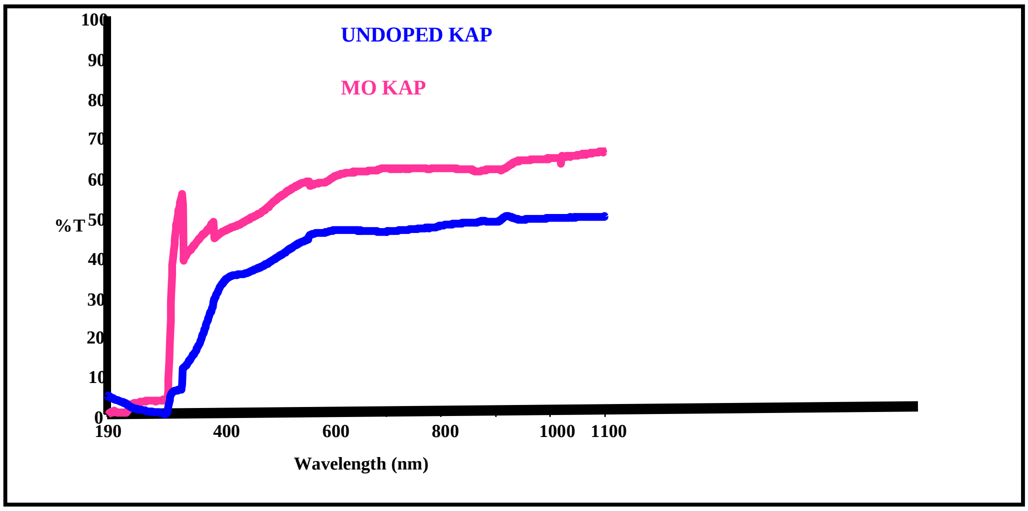

Figure No.4: (A) UV-Transmission spectrum of Undoped and methyl orange doped KAP crystal

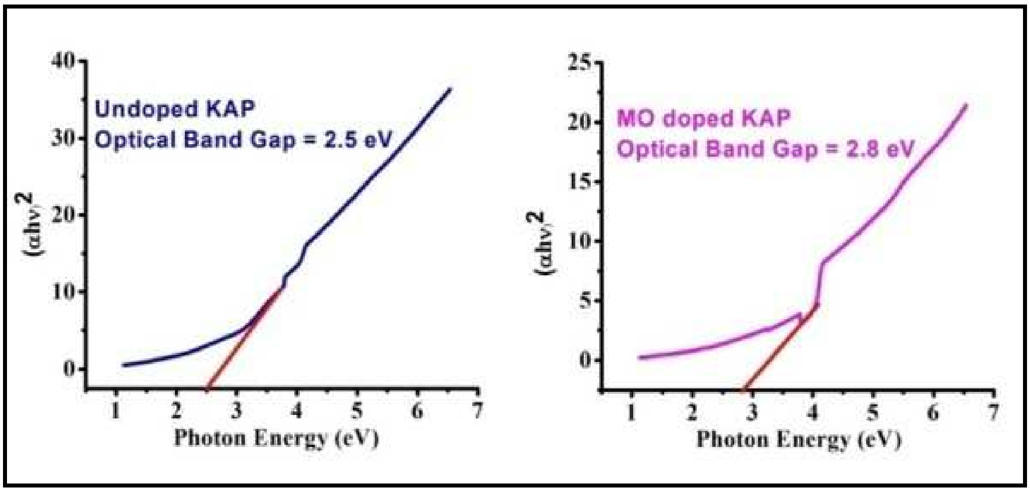

Figure No.4: (B) Tauc's plot for Undoped and Methyl Orange doped KAP crystal

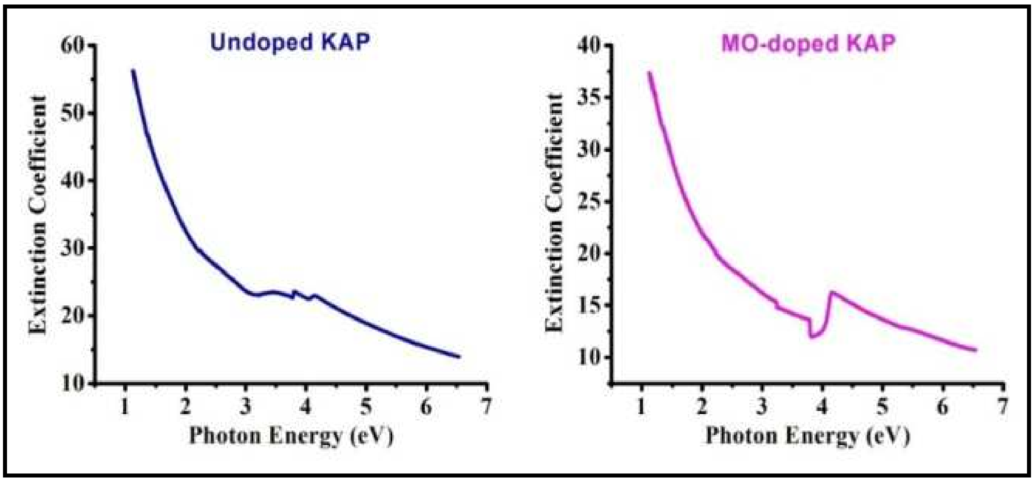

Figure No.4: (C) Plot of photon energy vs extinction coefficient for Undoped and Methyl Orange doped KAP crystal

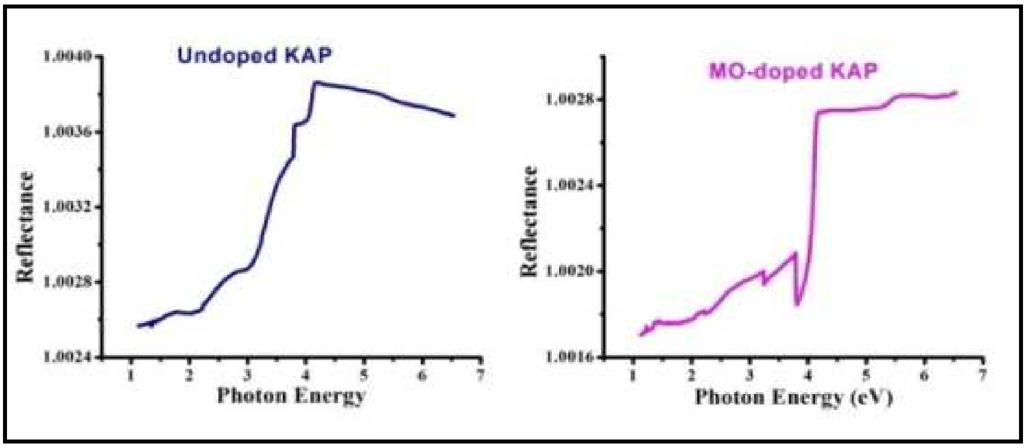

Figure No.4: (D) Plot of photon energy vs reflectance for Undoped and Methyl Orange doped KAP crystal

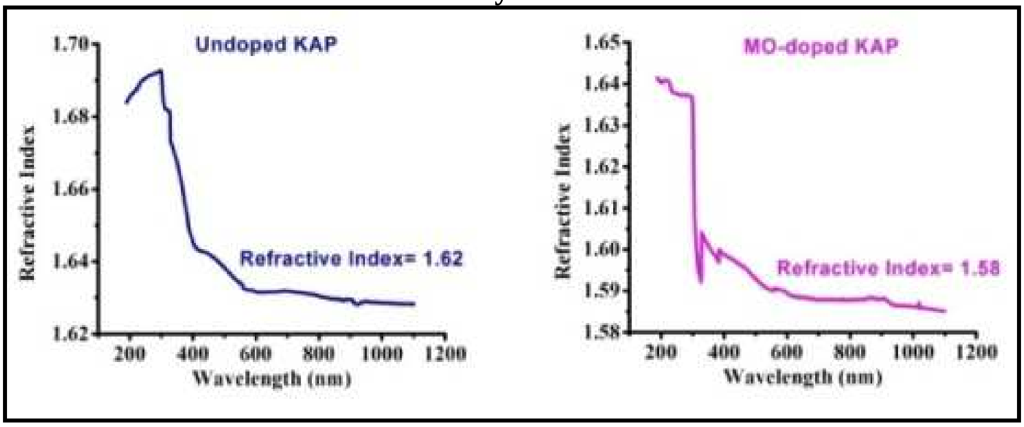

Figure No.4: (E) Plot of wavelength vs refractive index for Undoped and Methyl Orange doped KAP crystal

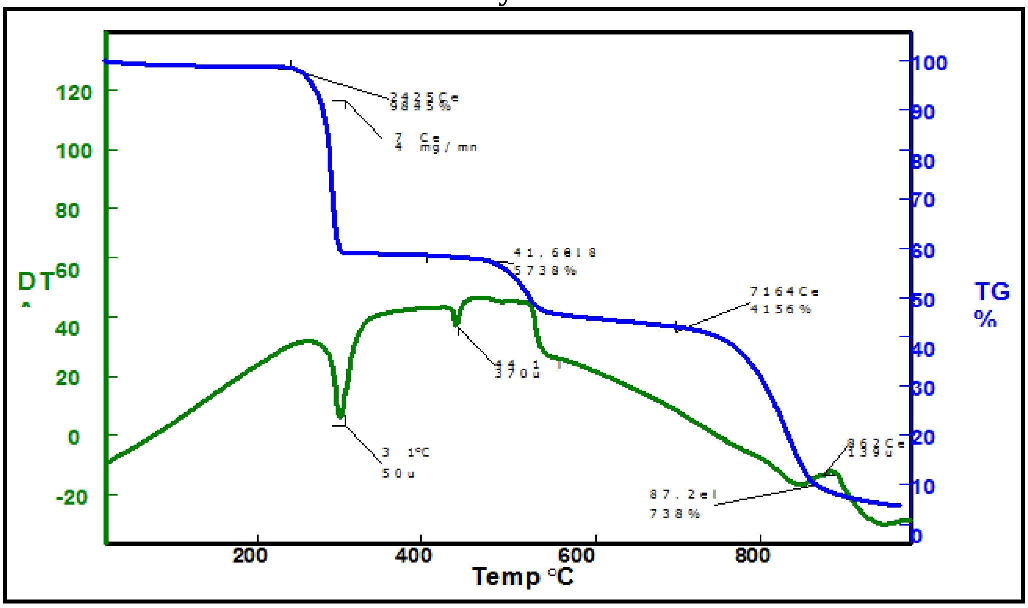

Figure No.5: TG/DTA thermo gram of methyl orange doped KAP crystal

Mechanical stability analysis

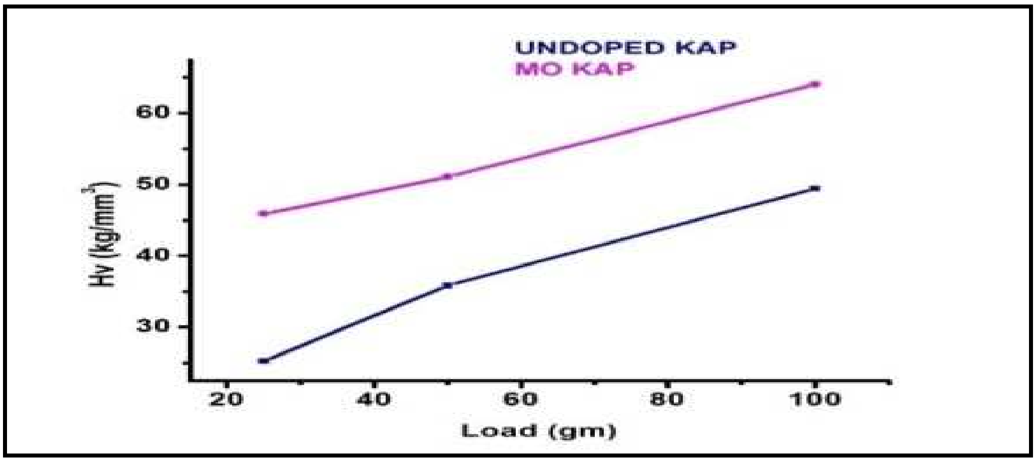

Figure No.6: Load vs H_v plot of Undoped and methyl orange doped KAP crystal

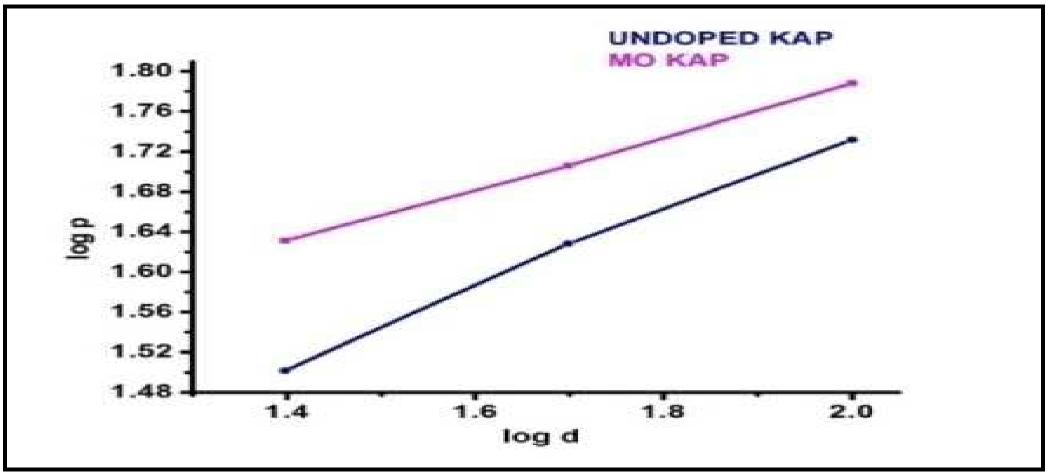

Figure No.7: Log p vs log d plot of Undoped and methyl orange doped KAP crystal

CONCLUSION

Undoped and Methyl Orange doped KAP crystals were grown by SEST. The structural parameters were evaluated by the single crystal XRD analysis and from the results it is known that both undoped and methyl orange doped KAP crystals crystallize in orthorhombic symmetery with a space group of $Pca2_1$. Powder XRD results suggest that both undoped and methyl orange doped KAP crystals are highly crystalline. The shifts in the peaks and the variation in the intensity of the peaks are due to the effect of the additive in the crystal lattice of KAP crystals. The FTIR spectrum confirms the presence of the functional groups present in the samples. The Optical Transmission spectrum confirms that the material is an eligible candidate for non linear applications. The doped specimen shows an absorption peak in the visible region due to which the sample is coloured. The SHG efficiency test was performed in order to study the NLO property of the crystal and it was found that dye doped KAP crystal has the NLO efficiency of 1.8 times that of KDP crystal. From the results it is concluded that dye doped KAP crystals serve as potential candidates for NLO applications.

ACKNOWLEDGEMENT

The authors gratefully acknowledge Dr. Babe Varghese, Head, SAIF IIT- Madras, Dr. Basheer Ahamed, B. S. Abdur Rahman University, Chennai and ACIC, ST. Joseph's College, Trichy for providing characterization facilities.

CONFLICT OF INTEREST

We declare that we have no conflict of interest.

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Please cite this article in press as: Seethalakshmi T. *et al*., Growth and characterization of methyl orange doped kap crystals - a potential material for optical and second harmonic generation applications, *International Journal* of *Research in Pharmaceutical and Nano Sciences*, 5(3), 2016, 164-175.