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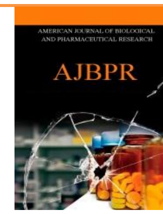

GROWTH AND CHARACTERIZATION OF PURE AND DISODIUM HYDROGEN PHOSPHATE MIXED WITH POTASSIUM DIHYDROGEN PHOSPHATE CRYSTAL BY USING SLOW EVAPORATION TECHNIQUE

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ABSTRACT

Potassium Dihydrogen Phosphate (KDP) is a well-known inorganic crystal. It has an interesting property such as Non Linear Optical (NLO), wide frequency conversion; high damage threshold against power laser and good UV transmission through its NLO coefficient and relatively low. It is more fashionable to all. Disodium hydrogen phosphate has been desired to dope in KDP. In present study single crystal of pure and disodium hydrogen phosphate mixed with KDP has been grown by slow evaporation solution growth technique. The crystalline and cell parameters were characterized by X-ray diffraction analysis, the shifting in frequency assignment of different functional groups of KDP due to addition of Disodium Hydrogen Phosphate (DSHP) were analyzed by FTIR analysis. By Using Vickers Micro-Hardness test the mechanical property of KDP crystal and disodium hydrogen phosphate mixed with KDP has been studied. The optical properties of the products were characterized by UV-Visible spectral analysis and Photo Luminescence spectroscopy (PL).

INTRODUCTION

KDP is a well-known inorganic nonlinear optical material, with unique ferro-electric, piezoelectric and electro-optic properties [1,2]. In recent scenario of information technology with fast, high density data storage, data retrieving, processing and transmission have demanded the research for new NLO materials in their single crystal form have wide applications in high energy lasers for inertial confinement fusion research [3], electro-optic switches, color display, frequency conversion etc [4]. Hence, there is a vast demand to synthesize new NLO materials and grow their single crystals, because most of the anisotropic physical, optical and electrical properties of the single crystals get deteriorated or completely diminished when these are not in the single domain crystal or have the defects like structural grain boundaries [5,6]. In parallel to discover the new NLO materials, it is also very important to modify the physical, optical and electrical, mechanical properties of these materials either by adding functional groups [7] or by incorporation of dopants [8-10] for tailor made applications. In the presence of dopants, growth promoting factors like growth rate [11] and many of the useful physical properties like optical transparency [12,13], Second Harmonic Generation (SHG) efficiency [9]

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and mechanical stability [10] get enhanced. The DSHP is an interesting inorganic NLO material. M. Gunasekaran published his work on growth and characterization of disodium hydrogen phosphate [14]. The growth quality and optical property of KDP crystals are affected by many factors such as additives and PH values [15].

Experimental Procedure

In the present work, double distilled water was used as the solvent for the growth of KDP crystal. Then the solution of KDP salt was prepared in a slightly under saturation condition. The solution was stirred well for two hours constantly using magnetic stirrer still the salt has been dissolved in water. Then the prepared solution was filter and transferred into a beaker and kept for crystallization at room temperature in a quiet place. After 24 days good quality single crystals of pure KDP has been harvested and the photographs are shown in Figure 1.

A supersaturated solution of pure KDP and disodium hydrogen phosphate mixed with KDP at room temperature has been prepared by same processes and then filtered into beaker. A slow evaporation method has been employed to grow KDP and disodium hydrogen phosphate mixed with KDP crystal. After 22 days the mixed crystals have been harvested and subjected to various characterizations viz, X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), UV spectroscopy, Vickers Micro-Hardness test and Photo Luminescence Spectroscopy the corresponding results have been compared with pure KDP crystal.

RESULTS AND DISCUSSION

Powder X-ray Diffraction (XRD)

The powder X-ray Diffractrometer analysis (XPERT-PRO) has been carried out for the rapid identification and quantification of grown crystal at 2θ position of 10^o to 80^o. The obtained results have been shown in figure 3 and 4. This study reveals that the grown crystal of KDP and disodium hydrogen phosphate mixed with KDP crystal belongs to tetragonal system. The crystal was identified by comparing the inter planer spacing and intensities of the powder pattern with the JCPDS data of KDP crystal. The calculated lattice parameter values are found to change as seen from Table 1. Mixing changes the cell axes and hence cell volume.

At maximum intensity the various structure parameters like the crystalline size, micro strain and dislocation density has been calculated by Debye- Scherer's formula and tabulated below [16-17].

FTIR spectrum studies

The qualitative aspects of infrared spectroscopy are one of the most powerful attributes of this diverse and versatile analytical technique. The Fourier Transform Infrared analysis has been carried out between 4000-400 cm^{-1} by recording the spectrum using KBR pellet technique. Figure 5 and 6 shows the FTIR spectra for pure and disodium hydrogen phosphate mixed with KDP crystals respectively and table represents the frequency assignment. The interaction and entry of the dopant into the lattice sites of KDP is clearly indicated by the absent and additional peaks and also by the broadening and shift in the vibrational absorption frequencies of the FTIR spectra.

The complexity of infrared spectra in 1450 to 600 cm^{-1} region makes it difficult to assign all the absorption bands, because of the unique patterns found there, it is often called the fingerprint region. Absorption bands in the 4000 to 1450 cm^{-1} region are usually due to stretching vibrations of diatomic units, and this is sometimes called the group frequency region.

O-H stretching due to water of crystallization arises at frequency of 3383cm^{-1} in pure KDP crystal. P-O-H bending and stretching arises at 2362 cm^{-1}andat 902 cm^{-1} in pure KDP spectrum, whereas in Disodium Hydrogen Phosphate (DSHP) mixed with KDP the bond arises at 2366 cm^{-1} and at 913 cm^{-1}. OH-asymmetric stretching arises at 3754 cm^{-1} and 2749 cm^{-1} in pure KDP spectrum, whereas in Disodium Hydrogen Phosphate (DSHP) mixed with KDP the bond arise at 2816 cm^{-1}.

The O=P-OH symmetric stretching vibration gives a strong band at 1652 cm^{-1} in pure KDP and at 1704 cm^{-1} in the mixed crystals. The C-N-H stretching vibration gives a band at 1299 cm^{-1} in pure KDP and at 1300 cm^{-1} in the mixed crystals. The appearance of peak at 1099 cm^{-1} for pure KDP and at 1087 cm^{-1} for DSHP mixed with KDP crystals are due to P=O stretching vibrations. The sharp peaks at 539 cm^{-1} for pure KDP and at 540 cm^{-1} for mixed crystals are due to HO-P-OH bending vibrations. N-H torsional oscillation arises in disodium hydrogen phosphate mixed with KDP crystal is at a frequency of 438 cm^{-1}.

Optical studies

The UV-Visible 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-Visible spectral analyses were performed to the grown crystals. Absorption spectra of NLO material play a major role in device fabrication [18].Wider the transparency window more will be the practical applicability of that material. The UV-Visible optical absorption and transmission spectra of the pure and disodium hydrogen phosphate mixed with KDP crystals were recorded in the wavelength range 190-1200 nm using Perkin Elmer UV-Visible NIR spectrometer (Model-Lambda 35).

The recorded absorption spectra are shown in Figure 7. From UV absorption pattern it is found that a strong absorption peak near the wavelength of 236 nm in pure KDP crystal.

Whereas in DSHP mixed with KDP crystal the absorption range is shifted towards the lower wavelength side around 203 nm. The change in the cutoff wavelength is due to the addition of disodium hydrogen phosphate which is of different in nature.

The optical band gap is obtained by plotting the graph between hυ and $(\alpha h\upsilon)^2$ as shown in figure 8 and 9. From the graph the optical energy gap of pure KDP is determined as 5.8 eV and disodium hydrogen phosphate mixed with KDP is determined as 6 eV.

For optical applications, especially for SHG, the material considered must be transparent in the wavelength region of interest .The recorded transmission spectra are shown in Figure 10. The spectra showing the 100% transmittance in both pure and mixed crystals .Both pure KDP and Disodium Hydrogen Phosphate mixed with KDP crystals have large transmission window in the entire visible region and the disodium hydrogen phosphate mixed with KDP crystal has higher transmittance compared to pure KDP crystal. As the entire region, it shows good transparency in the visible region so that it can be used for NLO applications. It is also seen that the cut of wavelength is almost same for pure and DSHP mixed with KDP crystals.

Micro-Hardness studies

One of the important properties of any device material is its mechanical strength represented by its hardness. Physically, hardness is the resistance offered by a material to localized plastic deformation (movement of dislocations) caused by scratching or indentation. The Indentation hardness is measured as the ratio of applied load to the surface area of the indentation. Indentation hardness measurement can, in principle, be carried out at fairly high loads (≈100g). But for materials which have low hardness and are available as small-sized sample, it is convenient to make measurements at low loads of less than 200g. The low load hardness is called micro-hardness [19]. Micro-hardness measurement is a general microscope technique for assessing the bond strength. The crystal slices [20] are well polished with a thickness variation less than 10μm.

The mechanical property of the grown KDP and disodium hydrogen phosphate mixed with KDP crystal were indented using HMV2T SHIMADZU micro-hardness tester filled with a Vickers pyramidal, intenter having an optical angle of 136^o between the opposite pyramidal. The indentation was measured as the ratio of applied load to the surface area of the indentation. Indentations were carried out using Vickers indenter at various loads from 25g to 100g. The static indentation has been made on the surface of the crystal and size of the impression is measured with aid of calibrated microscope.

The Vickers Micro-hardness has been calculated using the formula $Hv = 1.854(F/D^2)$. Load Vs Hardness number for KDP and disodium hydrogen phosphate mixed with KDP crystal is shown in figure 10. While comparing the disodium hydrogen phosphate mixed with KDP crystal with pure KDP, the hardness is high. At 100g the hardness number of KDP and disodium hydrogen phosphate mixed with KDP crystal is 28.35 Hv and 33.4Hv respectively.

Photo Luminescence studies

Photo luminescence characterization was done to reveal luminescent characterization of crystals for in-depth optical study. PL place as an additional confirmation tool to reveal the high electrical conductivity of the crystal by giving low intense spectra. Here photo luminescence study was carried out for pure KDP and KDP mixed with Di Sodium Hydrogen Phosphate (DSHP) at room temperature.

The recorded photo luminescence spectrograms for the samples were shown in figure11. If we compare the spectrum of pure KDP and Di Sodium Hydrogen Phosphate (DSHP) mixed with KDP a smaller blue shift was showed in disodium hydrogen phosphate mixed with KDP and also the photo luminescence intensity of the disodium hydrogen phosphate mixed with KDP was decreases. From low photo luminescence intensity we have confirmed that the obtained crystal have high electrical conductivity.

Table 1. Unit cell parameters of pure KDP and DSHP mixed with KDP crystal.

Crystal	a (Å)	b (Å)	C (Å)	Cell volume(Å) ^{3}
KDP	7.4362	7.4362	6.9703	385.437
KDP+DSHP	7.6278	7.6278	7.13258	414.997

Table 2. Shows the calculated structural parameters of KDP crystal, DSHP mixed with KDP crystal.

Sample	2θ (degree)	FWHM	Standard d-spacing (Å)	Strain η x 10-4	Grain size t(nm)	Dislocation density ρ x 1014 lines /m2
Pure KDP	23.914	0.090	3.71810	0.02201	16.868	0.0035143
KDP+ SHP	29.75	0.10	3.00082	0.02416	15.3669	0.004234

Table 3. Shows the functional group assignments for KDP and DSHP mixed with KDP frequency

Wave number (cm^{-1})		Vibrational Band Assignments
pure KDP	DSHP mixed with KDP	
3754	-	OH- asymmetric stretch
3383	-	O-H stretching hydrogen bond
2749	2816	OH- asymmetric stretching
2362	2366	P-O-H bending
1652	1704	O=P-OH stretch
1299	1300	C-N-H stretching
1099	1087	P=O stretching
902	913	P-O-H stretching
539	540	HO-P-OH bending
-	438	N-H torsional oscillation

Table 4 indicates that the hardness increase with the increase in load for all the crystals, without any cracks

Load(gms)	Hardness Number Hv (kg/mm^2)	
	KDP	KDP+DSHP
25	11.85	16.65
50	18.75	23.75
100	28.35	33.4

Figure 1. Photograph of as grown crystal of pure KDP

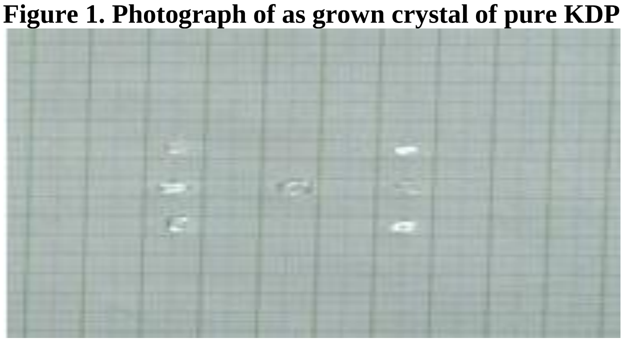
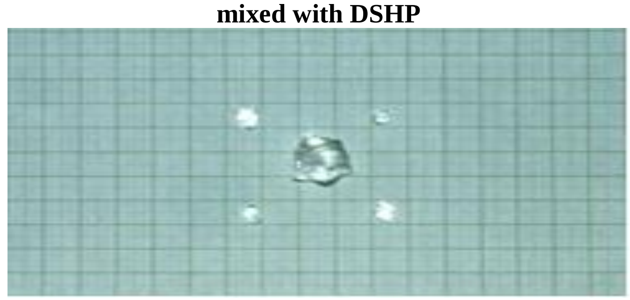


Figure 2. Photograph of as grown crystal of KDP mixed with DSHP



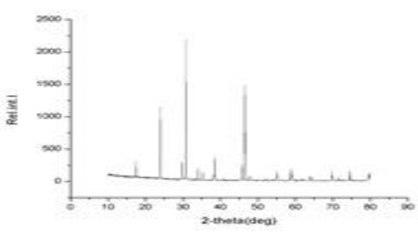


Figure3. Powder XRD pattern of pure KDP

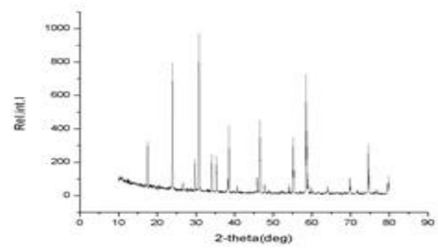


Figure 4. Powder XRD pattern of DSHP mixed with KDP

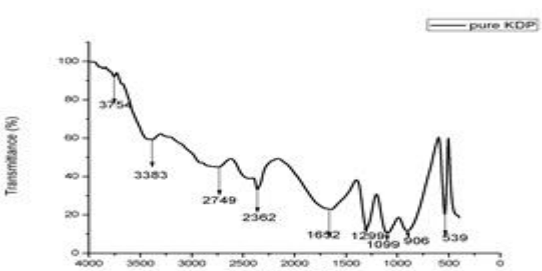


Figure 5. FT-IR spectrum studies of pure KDP crystal

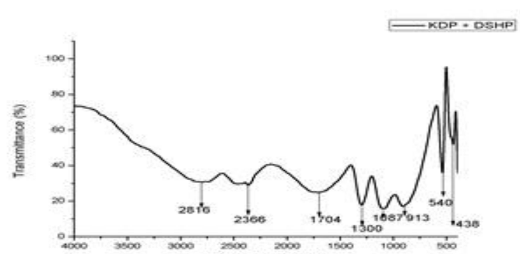


Figure 6. FTIR spectrum studies of DSHP mixed with KDP

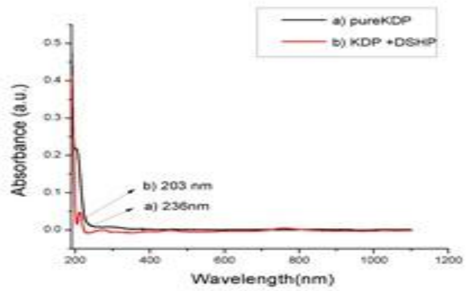


Figure 7. UV absorption spectrum of (a) pure KDP and (b) DSHP mixed with KDP crystals

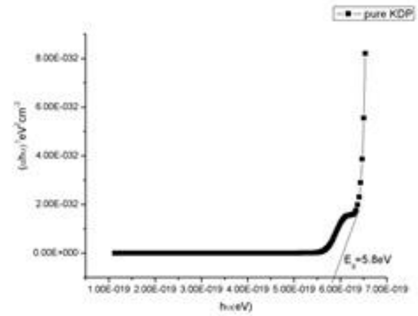


Figure 8. Plot of (αhυ)2 versus photon energy for pure KDP

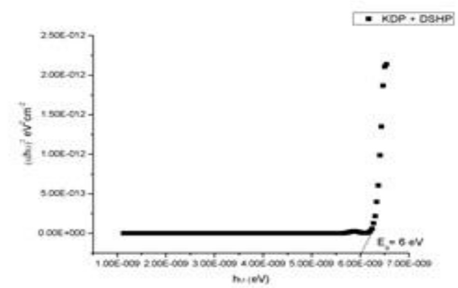


Figure 9. Plot of $(\alpha h\upsilon)^2$ versus photon energy for DSHP mixed with KDP

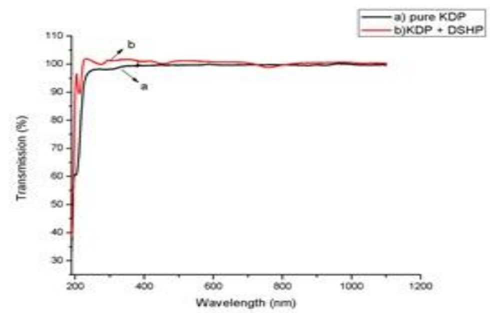


Figure 10. Transmittance spectrum of (a) pure KDP and (b) DSHP mixed with KDP crystals

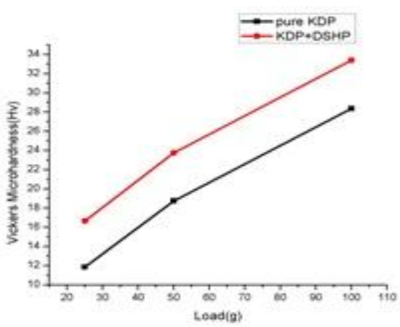


Figure 10. Vickers Micro-Hardness of grown crystal

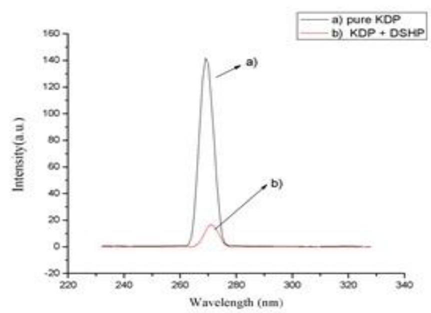


Figure 11. Photo Luminescence spectrums of pure KDP and KDP mixed with DSHP

CONCLUSION

KDP crystal is a queen of all crystals because of its high transparency and best NLO property. Additive of disodium hydrogen phosphate with KDP gives some changes in its basic character. Here the characteristic properties of pure KDP and disodium hydrogen phosphate mixed with KDP crystal has been investigated through FTIR, XRD analysis, UV-Visible spectroscopy, Vickers micro hardness test and PL has been studied. Pure and DSHP mixed with KDP crystals were grown by slow evaporation technique at room temperature. Colorless and transparent crystals were obtained. The powder X-ray diffraction studies, evaluation of lattice parameters confirms the dopants have gone into the lattice of the crystal and the crystal structure of KDP does not changed by doping of disodium hydrogen phosphate. The FTIR study confirms the presence of all functional groups and the addition of disodium hydrogen phosphate mixed with KDP crystal. The optical behavior is assessed by UV-Visible studies and it indicates the change in the cut off wavelengths. The shift of absorption and excellent transmission in entire visible region makes this crystal a good candidate for opto-electronic application. From micro hardness study, it was found that the hardness of disodium hydrogen phosphate mixed with KDP crystal has been improved. From PL the photo luminescence intensity of the DSHP mixed with KDP was decreases.

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