

Effect of copper thiourea complex on the performance of KDP single crystals

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A new semi-organic nonlinear optical (NLO) material metal thiourea complex doped KDP was grown in large size measuring $19 \times 5 \times 3 \text{ mm}^3$ by slow solvent evaporation technique for the first time. Optical quality KDP (KH_2PO_4) crystals can be grown by solution growth methods by conventional as well as fast growth techniques. Solution growth technique is followed for KDP and doped Copper Thiourea complex. KDP is an efficient angle tuned dielectric medium for optical harmonic generation in and near the visible region. Improvement in the quality of the KDP crystals and the performance of the KDP based devices can be realized with suitable dopants. The cell parameter values were determined by single crystal X-ray diffraction studies. Fourier Transform Infrared spectroscopic analysis was carried out on the grown sample to ascertain the fundamental functional groups. The thermal behavior of the grown copper thiourea complex doped KDP sample was analyzed by TG & DTA analysis. The mechanical properties of the grown crystals have been studied using Vickers microhardness tester. The optical transmission studies and second harmonic generation (SHG) efficiency studies justified the device quality of the grown crystal and the SHG study reveals that the grown sample has nearly 1.2 times higher efficiency than the potassium dihydrogen phosphate (KDP), a well known NLO material.

(Received May 29, 2007; accepted August 23, 2007)

Keywords: Growth from solution, Non-linear materials, Characterization

1. Introduction

One of the obvious requirements for a non-linear optical crystal is that it should have excellent optical quality. Potassium Dihydrogen Phosphate (KDP) is a model system for non-linear optical [1-5] device application. KDP is an efficient angle tuned dielectric medium for optical harmonic generation in and near the visible region. This material offers high transmission throughout the visible spectrum and meets the requirement for optical birefringence, large enough to bracket its refractive index for even extreme wavelength over which it is transparent. Among the non-linear optical phenomena, frequency mixing and electro-optics is important in the field of optical communication. Improvement in the quality of the KDP crystals and the performance of the KDP based devices can be realized with suitable dopants. To analyze the influence of metal ions thiourea complex based dopants on the non-linear optical property of KDP crystals, efforts were made to dope Copper Thiourea complex in KDP single crystals. Optical quality KDP (KH_2PO_4) crystals can be grown by solution growth methods by conventional as well as fast growth techniques. Mechanical and non-linear properties of the doped crystals were studied with the characterization studies such as powder XRD, FTIR, UV-Visible, SHG measurements respectively.

In this view we are presenting the single crystals of copper thiourea complex doped KDP, which have been grown for the first time. It is a potential semi-organic NLO material. The optical quality copper thiourea complex doped KDP crystals have been grown by the slow

evaporation method. The grown crystals were characterized by single crystal X-ray diffraction, FTIR, TG & DTA and UV-VIS-NIR spectroscopy. SHG efficiency of the grown sample was measured by powder Kurtz method using Nd:YAG laser.

2. Experimental details

2.1 Crystal growth

Pure KDP and doped KDP crystals were grown from aqueous solution by slow evaporation. The same method is followed for doped KDP crystals (0.1 mole % of Copper Thiourea complex). The solubility of doped KDP in the solvent was measured for each dopants, it was found to be 31.5 gms/100 ml at 40 °C for KDP and 32.75 gms/100 ml at 40 °C for Copper Thiourea complex. The seed crystals are prepared at low temperature by spontaneous nucleation. The seed crystals with perfect shape and free from macro defects were used for growth experiments. Large single crystals KDP and doped KDP (Copper Thiourea complex) were grown using constant temperature bath (CTB) controlled with an accuracy of 0.01 °C. The growth process is initiated in the experiments by inserting the KDP seed into its supersaturated solution [6-7] and is followed by slow cooling of the solution. A supersaturated solution of KDP powder is prepared in distilled, deionized water. The amount of KDP salt to be dissolved is determined from its solubility curve at an average temperature of 38 °C. The solution is stirred long enough to ensure complete dissolution of the solute, and filtered using Whatman-100 filter paper is maintained at relatively

high temperature for about 4-5 hours using circulation from the temperature control unit. Subsequently the solution is cooled by applying a suitable ramp rate, 0.1 °C /day in the present study. When the solution reaches a value right enough for becoming saturated, a KDP seed is introduced in to the solution using a thin nylon thread. The orientation of the seed crystal is adjusted in such a way that the prismatic faces {100} are placed normal to the direction of the laser beam. Experiments are allowed to run for considerably longer duration of the time (20 days) in order to allow the growth of large crystals.

The solubility of doped (0.1 mole % of Copper Thiourea complex) KDP have been determined for different temperatures, 30, 35, 40 and 45 °C. The solubility for doped KDP in water was determined for two different pH values, 4.45 and 4.75. The solubility was determined by dissolving the solute in water in an airtight container maintained at a constant temperature with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The same process was repeated for the doped KDP solutions.

2.2 Characterization studies

Powder X-ray diffraction studies were carried out for the as grown crystals using Rich Seifert X-ray diffractometer with CuK α ($\lambda = 1.54598$ Å) radiation. The FT-IR spectra of all the crystals were recorded from solid phase samples on a Bruker IFS 66V model spectrophotometer using 1064 nm output of a cw diode pumped Nd:YAG laser as a source of excitation in the region 400 – 4000 cm⁻¹ operating at 200 mW power at the samples with a spectral resolution of 2 cm⁻¹. The IR spectra were also recorded on Shimadzu-800, FTIR spectrometer series of Japan in the region 400 – 4000 cm⁻¹. The UV-VIS spectrum of KDP, doped KDP crystals were taken in the wave length 200 nm - 1200 nm range using the Varian CARY5E UV-VIS-NIR Spectrophotometer. Kurtz SHG test was performed to find the non- linear optical property of KDP.

Table 1. Comparison of NLO properties of pure and doped KDP crystals.

S.No.	Compound	NLO efficiency
1.	KDP	1.00
2.	Thiourea	1.92
3.	Cu Thiourea complex doped KDP	2.34

3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction studies have been carried out to confirm the crystallinity and to calculate the lattice parameters of the grown samples [Fig. 1.(a), 1.(b)].

Using the monoclinic crystallographic equation, the lattice parameter values of doped KDP crystals were calculated and compared with the literature values [9]. The calculated values are in line with the literature value. The calculated lattice parameter values are of $a = 18.68$ Å, $b = 5.21$ Å, $c = 7.21$ Å and $\beta = 101.7^\circ$. This confirms that the doped KDP single crystal retain its own crystal system.

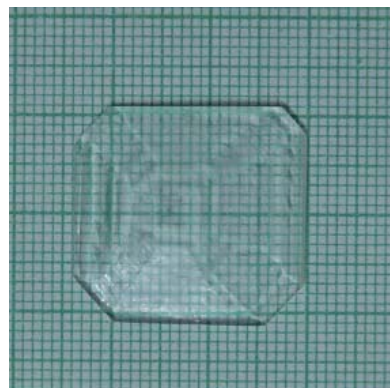


Fig. 1(a). Pure KDP crystal.



Fig. 1(b). Cu Thiourea doped KDP crystal.

3.2 FT-IR studies and UV-visible studies

Due to the greater mass (Fig. 4) of sulfur the C=S vibration is expected to occur at considerably lower frequencies than the C=O vibration, in the C-O or C-N region. The comparisons of FT-IR studies on pure and Cu thiourea complex doped KDP crystals are shown in Table 2. This result that more than one band involves C=S stretching. In thioamides the NH₂ rocking vibration can also interact. Vibrational analysis reveals that thioformamide has a band at 800 cm⁻¹ which is almost pure C=S stretching, but that in other thioamides much mixing occurs. Bands have been assigned as involving C=S stretching at 1420-700 cm⁻¹. Thioacetamide has bands 718, 975 and 1308 cm⁻¹ involving C=S stretching. UV-visible spectra for dyes (Fig. 2 & Fig. 3) doped shows that the Cu thiourea complex enhances the optical property of KDP crystal. After incorporation of Cu, the UV absorption was shifted to blue region. The blue shift increases in accordance of mole fractions of dopants. The pure KDP crystal has about 80% of transmission. The Cu thiourea

doped crystal is invariably has higher transmission percentage compared to pure KDP crystal. In the spectrum, transmission percentage increases due to additive of thiourea in KDP crystal.

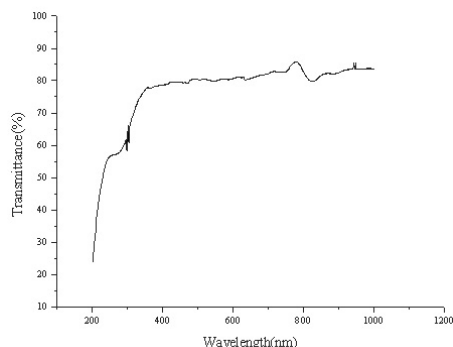


Fig. 2. Transmittance of pure KDP crystal.

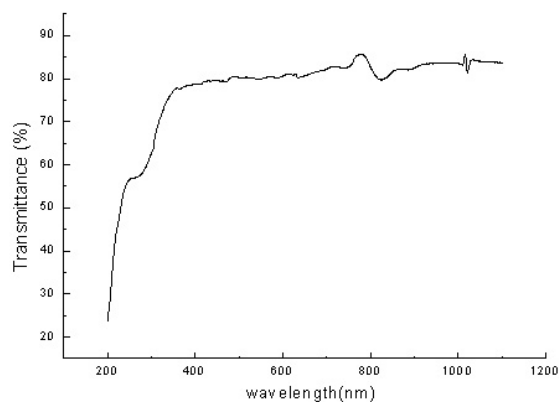


Fig. 3. Transmittance of Cu Thiourea complex doped KDP crystal.

Table 2. FT-IR Assignments of Pure and Cu Thiourea Complex Doped KDP single crystals.

Calculated frequency (cm ⁻¹)	Pure KDP	KDP + Cu	Assignment
3731	3801(VW)	3778(VW)	Free O-H stretching hydrogen bonded of KDP
3657	3608(W)	3619(W)	O-H asymmetric stretching
3605	3625(W)	3611(VW)	O-H symmetric stretching
3388	-	3375(W)	N-H Hydrogen bonded stretching
3333	-	3350(S)	Aliphatic stretching superimposed with N-H stretching
3301	-	2990(W)	N-H asymmetric stretching in NH ₂ group
3108	-	3100(W)	N-H symmetric stretching in NH ₂ group
3066	3075	3061(M)	NH ₂ superimposed with P-O-H stretching
2461	2475(M)	2475(M)	P-O-H bending of KDP
2358	2325(W)	2330(W)	May be due to dopant of either Cd (or) Pb
1861	-	1900(W)	C-N stretching
1600	1633(VS)	1650(VS)	O P – OH stretching of KDP
1503	-	1510(VW)	N-H in-plane bending
1350	-	1350(S)	May be due to dopant of either Cu (or) Zn
1295	-	1261(VW)	C-N-H deformations
971	1101(S)	1099(S)	P-O-H stretching of KDP
858	-	863(VW)	N-H Wagging
790	-	781(VW)	C-N stretching
621	-	625(VW)	Cu-O-P=O stretching
543	5509(VS)	539(VS)	HO-P-OH bending
480	-	481(M)	N-H torsional oscillations

VS – Very Strong S – Strong M – Medium W – Weak VW – Very Weak

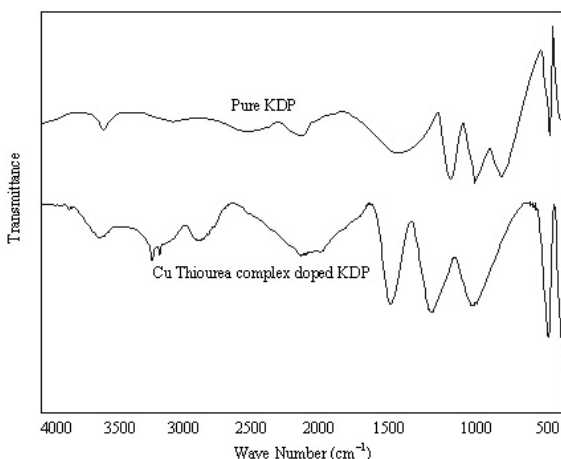


Fig. 4. Observed FTIR spectra of single and doped KDP.

3.3. Thermal studies

Fig. 5 illustrates the differential thermal analysis (DTA) and thermo-gravimetric analysis (TGA) curves for the grown Cu thiourea doped KDP samples. The DTA curve implies that the material undergoes an irreversible endothermic transition at 200 °C where the melting begins. The peak of the endothermic [11-14] represents the temperature at which the melting terminates which corresponds to its melting point at 210 °C. Ideally, the melting point of the trace corresponds to a vertical line. The TG curve of this sample indicates that the sample is stable up to 220 °C and above this temperature; the weight loss is not due to self-degradation of doped KDP but merely to its evaporation after its melting. The sharpness of the endothermic peak shows good degree of crystallinity of the grown ingot. The endothermic peak at 250 °C indicates a phase change from liquid to vapor state as evident from the loss of weight in TG curve.

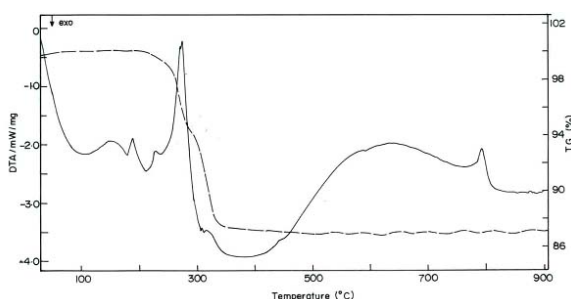


Fig. 5. TGA-DTA of doped KDP crystal.

3.4. Second harmonic generation efficiency measurements

The second harmonic generation (SHG) conversion efficiency of doped KDP was measured by the powder

Kurtz and Perry [15-17]. The crystal was ground into a homogeneous powder of particles and densely packed between two transparent glass slides. A Q-switched Nd:YAG laser beam of wavelength 1064 nm (pulse width 8 ns) was allowed to strike the sample cell normally. The SHG output (532 nm) was finally detected by photomultiplier tube. A sample of potassium dihydrogen phosphate (KDP), also powdered was used for the same experiment as a reference material in the SHG measurement. It is found that the frequency doubling efficiency of the doped KDP is better than KDP. A comparison of NLO property of doped KDP crystal with a few well-known NLO crystals is presented in Table 1.

3.5 Mechanical properties

Hardness is one of the important mechanical properties of the materials. It can be used as a suitable measure for the plastic properties and strength of a material. Microhardness measurements were carried out using Leitz Weitzler hardness tester fitted with a diamond indenter. The well-polished doped KDP crystal was placed on the platform of the Vickers microhardness tester and the loads of different magnitudes were applied over a fixed interval of time. The indentation time was kept as 8 s for all the loads. The hardness was calculated using the relation $H_v = (1.8544 * P)/(d^2)$ kg/mm², where P is the applied load in kg and d is the diagonal length of the indentation impression in micrometer. The hardness decreases gradually with the increase of load and above 35 gm cracks develop on the smooth surface of the crystal due to the release of internal stresses generated locally by indentation. The hardness of doped KDP value is less than the other semi-organic crystals.

4. Conclusions

Good optical quality single crystals of semi-organic doped KDP have been grown from solution by slow solvent evaporation technique for the first time. A new nonlinear optical material, Cu thiourea complex doped KDP crystals have been grown by slow evaporation technique at room temperature. The functional groups present in the grown crystals have been confirmed by FTIR spectral analysis. The observed frequencies were assigned on the basis of symmetry operation on the molecule and normal coordinate analysis. The crystallinity of the grown sample was confirmed by single crystal X-ray diffraction analysis. Various functional groups present in the grown crystal were identified by FTIR spectroscopy. Thermal stability of the grown sample was studied by TG & DTA analysis.

TG curve of this sample indicates that the sample is stable up to 210 °C. Optical transmission range of doped KDP is measured to be 200–1200 nm, i.e. the grown doped KDP crystal has a good optical transmission in the entire visible region. The powder SHG measurement shows that the grown doped KDP crystal has 1.2 times higher NLO efficiency than KDP. Vickers micro hardness was

calculated in order to understand the mechanical stability of the grown crystals.

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