

GROWTH AND STRUCTURAL ANALYSIS OF DOPED KDP CRYSTALS: GEL TECHNIQUE

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ABSTRACT

The growth of doped KDP crystals was initiated at room temperature using gel technique. Hydrosilica gel medium was prepared with the help of Sodium Metasilicate (SMS) solution mixed with weak acid i.e. Acetic Acid. The Oxalic Acid used as dopant, caused slight shift in the frequency of functional group present in pure KDP, which was studied by Fourier Transform Infrared Spectroscopy (FTIR). The lattice parameters of the grown doped crystals were determined by powder X-ray diffraction pattern (XRD). Further the Oxalic Acid doped KDP crystals were subjected to Thermogravimetric Analysis. The melting point and decomposition temperature was determined from this TGA/DTA characterization.

Keywords: KDP, Oxalic Acid, Hydrosilica gel medium, FTIR, XRD, TGA/DTA

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INTRODUCTION

“Gels (of silicic acid, agar, gelatine etc.) form excellent media for the growth of crystals of almost any substance under absolutely controllable conditions that approach perhaps more closely those of nature, except for temperature and pressure, than any other laboratory method”¹. This technique of growing crystals is century old. The properties of gel such as the presence of large number of fine pores in it, highly viscous two component system of a semisolid nature and transparency have made gel an excellent medium for crystal growth. The formation of gel for the growth of crystals along with its properties was discussed by Heinz K. Henisch². Potassium Dihydrogen Phosphate (KDP) is best known for its nonlinear optical (NLO) property. In an attempt to improve its NLO property, many researchers have doped KDP crystals with different organic and inorganic substances. Besides NLO property KDP has high birefringence, high damage threshold and very good UV transmission. All these properties of KDP have paved its path in commercial as well as non-commercial applications.

The effect of L-Lysine in pure KDP crystal was studied. L-lysine mono hydrochloride amino acid was added to KDP solution and crystals were obtained by slow aqueous solvent evaporation technique³. Using slow evaporation technique, KDP doped with L-alanine crystals were initiated at room temperature⁴. KDP crystals with Potassium Chloride (KCl) and Ethylene Diamine Tetraacetic Acid (EDTA) as dopants have been reported⁵. L-arginine trifluoroacetate (LATF) was used as an additive for pure KDP crystals. These doped KDP crystals were obtained by slow evaporation technique⁶. In the present investigation, Oxalic acid was used as a dopant for pure KDP. These crystals were prepared at room temperature in Hydrosilica gel medium.

EXPERIMENTAL

Preparation of Hydrosilica gel

31 gm of Sodium-Metasilicate (SMS) powder was allowed to dissolve in 30 cc of double distilled water. This solution of SMS was continuously stirred with the help of magnetic stirrer. The solution was allowed to precipitate and clear SMS solution was obtained by filtering it through Whatmann filter paper. The specific gravity of clear SMS solution was maintained at 1.17 by using specific gravity bottle technique. This clear SMS solution obtained was basic in nature. For the preparation of gel an acidic medium was required. Hence a weak acid i.e. Acetic Acid was added drop by drop till pH reached 6. The pH was not

maintained 7 because gel would solidify at once. Once the pH was maintained, SMS solution was poured in a test tube and mouth of the test tube was covered by cotton plug. Gelation process was not elicited immediately.

Preparation of KDP + Oxalic Acid solution

1 molar concentration of oxalic acid was prepared. The oxalic acid solution was mixed with KDP solution in the ratio 3:1 i.e. (KDP): (Oxalic acid) was 3:1. The clear solution was poured at the top of the Hydrosilica gel drop by drop. Since the gel is in semi-solid state, KDP + oxalic acid solution did not enter the gel medium immediately. It slowly passed through the pores of the gel.

The process of crystal growth was not immediately triggered, when the clear solution of KDP + oxalic acid was added to it. It was a gradual slow process. Since Hydrosilica gel is transparent, the interaction between KDP and oxalic acid could be observed at every stage.



Fig.-1: Grown crystals of KDP + Oxalic Acid

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FTIR)

The presence of Oxalic Acid and KDP in the grown crystals was confirmed by FTIR Spectroscopy, which showed peaks of corresponding functional groups. Since KDP and Oxalic Acid are used, mainly the presence of C=O, P=O, phosphonic acid (O=P-OH) and O-H group are expected. The transmittance (%) versus wavelength (cm^{-1}) graph is shown in figure-2. This analysis was carried out between 3500 – 500 cm^{-1} wavelength.

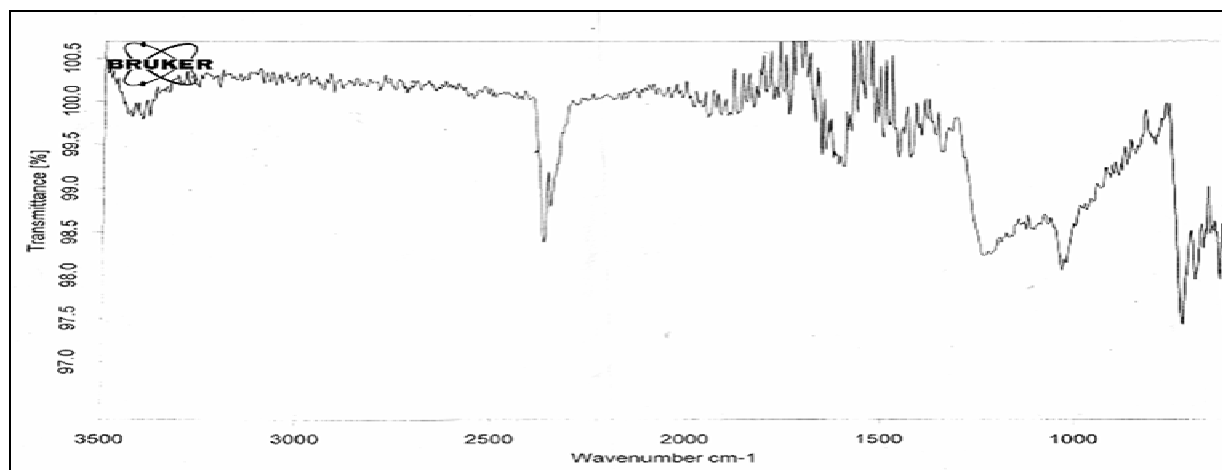


Fig.-2: Transmittance versus wavelength graph of FTIR spectroscopy

The interpretation of the FTIR spectrum is given in table-1. There are very few assignments of Oxalic Acid present in the obtained spectrum, compared to those of KDP. This demonstrates that Oxalic Acid is present in small quantity in the grown crystals, as it is to be expected since it was added as a dopant to pure KDP.

X-Ray Diffraction Characterization

The grown crystals of KDP + Oxalic acid were subjected to powder X-ray diffraction analysis. Bragg peaks were obtained at particular 2θ values. The intensity versus 2θ graph is shown in figure (3). Obtained crystal belongs to tetragonal crystal structure. The lattice parameters of grown crystals were determined using POWD – an Interactive Powder Diffraction Data Interpretation and Indexing Program. They were calculated as $a = b = 7.400 \text{ \AA}$ and $c = 6.880 \text{ \AA}$. Lattice parameters of pure KDP crystals are $a = b = 7.452 \text{ \AA}$ and $c = 6.974 \text{ \AA}$. This demonstrated that the obtained diffraction pattern shows inconsequential fall of lattice parameters 'a' and 'c' of the grown crystals.

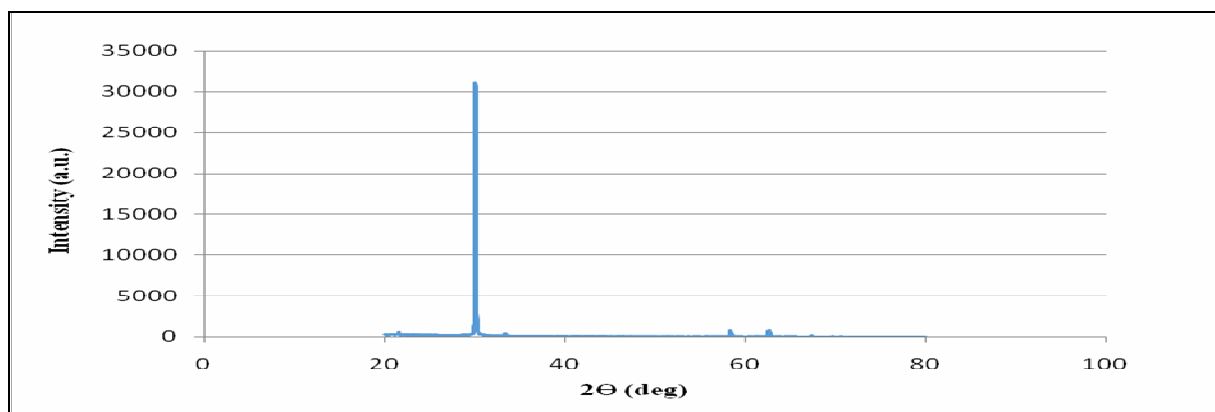


Fig.-3: XRD Pattern of Doped KDP Crystal

Thermogravimetric analysis& Differential thermal analysis

Perkin Elmer instrument was used to carry out TGA and DTA analysis of the grown crystals. This analysis has been carried out between 25-900 °C temperature ranges at a heating rate of 20 °C/min. The TGA and DTA graphs are represented in figure-4 and figure-5 respectively.

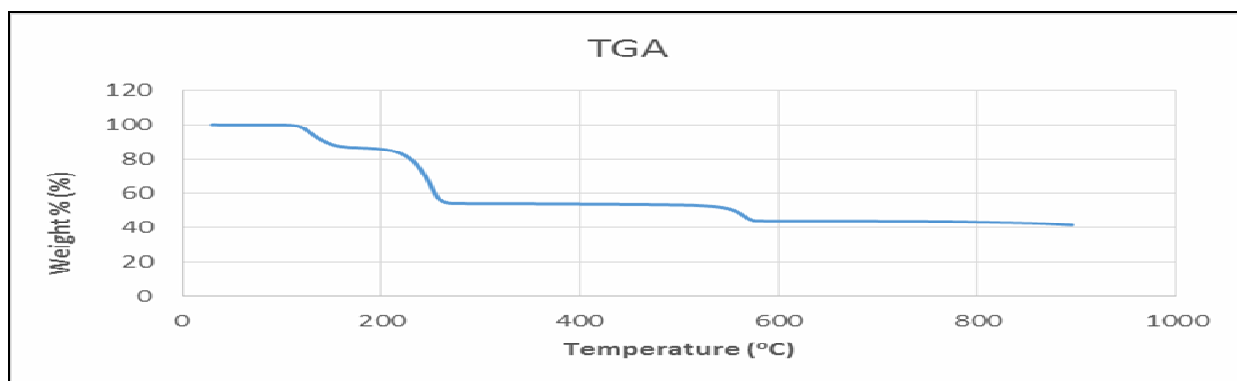


Fig.-4: TGA graph

The melting point and decomposition temperature of the sample are illustrated in table-2. The TGA graph shows two stages of decomposition. The first stage is obtained at 200 °C and the second is at 530 °C. The

same is attained in DTA graph, which shows the first stage of decomposition at onset temperature 227.60 °C and the second stage at onset 540.49 °C.

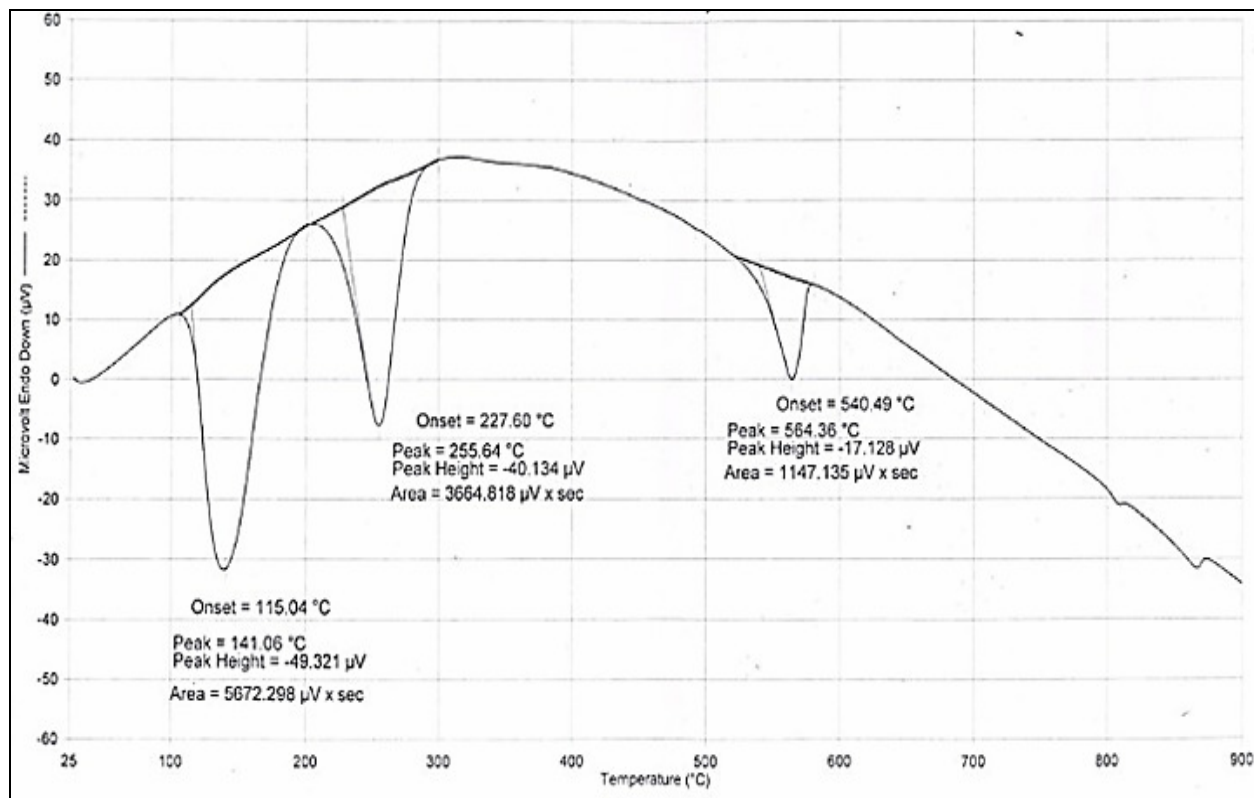


Fig.-5: DTA graph

Table-1: Interpretation of FTIR spectroscopy

Frequency in cm^{-1}	Functional Groups Assignments
3220	O-H stretching , H bounded
3100	O-H stretching
2930	O-H stretching
2540	O=P-OH phosphonic acid
1730	C=O stretching, H bounded
1650	O-P-OH symmetric stretching
1470	O-H stretching
1230	P=O stretching
1110	P=O stretching
900	C-O stretching
840	O=P-OH bending
720	HO-P-OH bending

CONCLUSIONS

The gel technique of growing crystals is very slow process, but this process yields good quality of crystals. In the preparation of gel, pH of the solution plays a vital role. For good quality of gel, pH between 5 and 6 is desirable. The results obtained from FTIR spectroscopy confirmed the presence of Oxalic Acid in pure KDP. TGA and DTA characterization reveals multi-stage decomposition of the

grown crystals. XRD data reveals no change in the crystals structure, when Oxalic Acid is added as a dopant to pure KDP. This gives an impression that KDP is more dominant over Oxalic Acid.

Table-2: TGA/DTA Analysis of Doped KDP crystal

Sample	Thermogravimetric analysis (TGA)		Differential Thermal Analysis (DTA)			
	Melting Point	Decomp. Temp	Melting Point	Nature of Peak	Decomp. Temp.	Nature of Peak
KDP + Oxalic Acid	110 °C	200 °C	115.04 °C	Endothermic	227.60 °C	Endothermic

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