Growth of L-Valine Potassium Dihydrogen Phosphate Bulk Single Crystal by Sankarnarayanan-Ramasamy (S-R) Method

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ABSTRACT : Optically transparent non linear crystal of potassium dihydrogen phosphate (KDP) has been grown by solution as well as SR method. The crystal grown form solution methods have excellent transparency was confirmed by UV-visible spectrum which shows 90 % transmittance; and lower cut off wavelength is 224 nm. The crystal grown by SR method along (101) plane was observed with growth rate 3mm per day for 15 days and dimension reached up to 50 mm in height. The functional groups were identified by FTIR analysis, further the grown crystals were characterized by TGA/DTA analysis, which reveals that the crystal were thermally stable below of 220^{0}C. The higher concentration of amino acid dopant increases the hardness value crystal. At 50 g the Hv of doped KDP was found to be 120.4 *Hv* and 122.0 *Hv*.

Key Words - UV-Vis studies, growth form solution, Hardness.

1. Introduction

The remarkable investigations have been carried out in past decades to develop Non Linear Optical (NLO) single crystal which was based on optoelectronics, acousto-optics, Laser, Telecommunication Technologies, Medical Instrumentation etc.[1, 2]. Large size KDP single crystal possesses important piezoelectric, ferroelectric, electro-optic and mainly NLO properties. Such demand requires the rapid growth of crystals in a shorter duration of time while maintaining the quality and size. Harvesting of such bulk size crystals is still continuing [3, 4]. The best transparent dielectric materials are KDP for its nonlinear optical properties and electro optical properties. Because of its nonlinear optical properties, it has been incorporated into various laser systems for harmonic generation and optoelectrical switching [5].from this point of view the SR method has been used to grow KDP crystal with specific orientation in an ampoule. Study reveals that the only amino acid single crystals possess wide transparency in UV–visible region [6,7] and it is better for second harmonic non-linear optical (NLO)- application-based devices.

In this work we have reviewed the growth mechanisms, process and method adopted to grow good quality transparent single crystals by sankaranarayanan ramasamy (S-R) method.

Review

The Literature review showed that the advanced laser imaging, optical communication and data storage systems require improved nonlinear optical materials of KDP which was achieved by doping amino acid as dopant in mother solution of KDP. This is turn improves the optical, thermal etc. properties of KDP. Organic impurities enhance the NLO properties and hence in this work we have presented the 2 amino-3methylbutanoic amino acids (valine) doped Potassium dihydrogen phosphate (KDP) crystal. And confirmed the strong interaction of L-valine with the –OH group of KDP.A comparative study was carried out on L-valine amino acid doped potassium dihydrogen phosphates (KDP). Pure and doped transparent bulk single crystals were successfully grown by above mention methods. The dopant concentration was 0.6, 0.8, 1.0, and 2.0 mole % in mother solution.

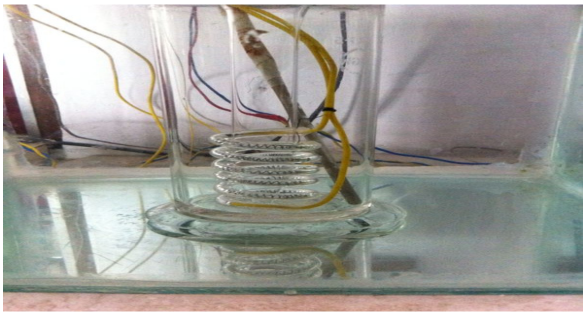

Figure 1 .Modified CTB in S-R method (using Spiral glass tube)

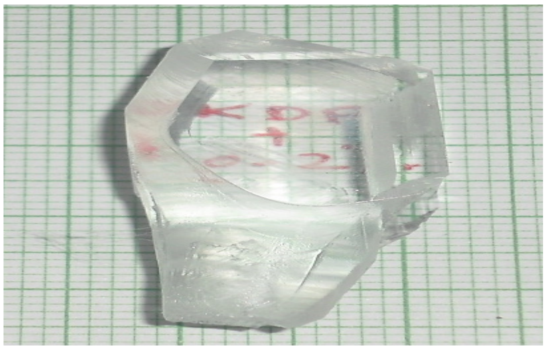

Figure 2. Grown crystal by S-R method

2. Methods

2.1 Growth rate for SR method: A glass ampoule was designed and fabricated at laboratory for the growth of KDP single crystal, by modifying the CTB of SR method. In present investigation single crystal of LVKDP were grown from its aqueous solution by solvent evaporation method and modified CTB (constant temperature bath) of S-R method. Especially design Spiral glass tube shown in Fig.1 was used to surround the bottom of glass ampoule to maintain constant temperature during growth of crystal. For this first seeds was prepared [8, 9] by slow cooling and slow evaporation of saturated solution in a clean controlled temperature enclosure. A clean defect frees Seed along (100) plane which was fixed by mounted at the bottom of the ampoule in such a way that the seed should be tight at the end of ampoule to avoid bidirectional growth of crystal from the surround area of crystal. The ring heater was connected to the temperature controller and it provides the optimum heat. The face was exposed to the solution of LVKDP so that the growth of bulk size crystal can be initiated. The solvent get was saturated using pH- 4.8 for L- valine (P. Kumaresan *et al.*2008). The top open face of the ampoule was covered by a thick plastic sheet with a hole at the center for facilitating controlled evaporation of the solvent. The whole setup was placed in a zero vibration zone area. After 15 days a good quality transparent crystal of LVKDP was observed with growth rate 3mm per day for 15 days and dimension reached up to 50 mm in height is shown in Fig. 2

3. Result

3.1 UV –VIS spectral analysis: Single crystals are mainly used in optical application. Hence the UV-Vis-NIR spectral transmittance was studied using a model Varian, Cary 5000 spectrophotometer with a single crystal of 5 mm thickness in the range of 200 – 1600 nm. The recorded spectrum is shown in Fig. 3. From figure it is observed that the percentage of optical transmission increases with the increase of concentration of L-valine in KDP crystals. The result of L-valine doped KDP have good agreement with the result reported [8]. The crystal has sufficient transmission in the entire visible and IR region. The lower cut off wavelength is around 224 nm; the transmission percentage of valine doped KDP crystal is around 90 %.

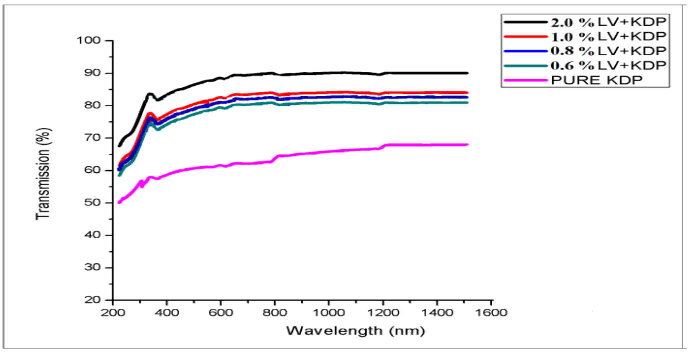

Figure 3. Uv-vis pattern of pure KDP and LV+ KDP

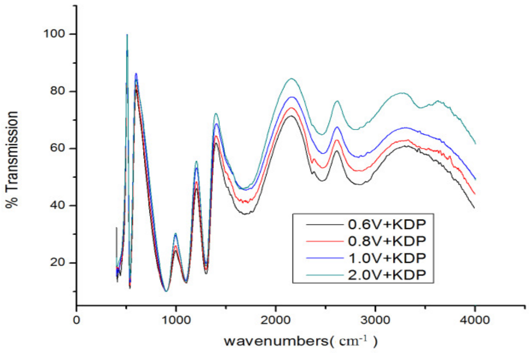

Figure 4. FTIR Spectra of LV+ KDP

3.2 FTIR analysis : The vibration spectra were recorded in the region of range 400-4000 cm $^{-1}$ using a Thermo Nicolet, Avatar 370 FTIR spectrometer by KBR beam splitter. The pure KDP crystal was studied by FTIR by O. V. Mary Sheeja *et. al*[10]. Form this observation it is confirmed that effect of organic amino acid on Pure KDP which gives additional peaks corresponding to the functional groups of L-valine. The vibration frequencies of functional groups of L-valine used in KDP crystal has been identified by FTIR spectroscopy is as shown in Fig. 4. The FTIR spectra of pure KDP [11] and KDP doped with valine shows that the slope band in the high energy region is due to free O–H stretching of water, P–O–H group of pure and L- valine doped KDP (P. Kumaresan et al.,2008). By comparing these graphs it reveals that there is high similarities, it means that pure KDP peaks are predominant over valine peaks due to the low amount of doping valine in the compound compared to pure KDP. These vibrations of amino acids present in the spectra of doped crystals reveals the incorporation of impurities in the crystals. (B Suresh Kumar *et al.*2008) and the corresponding wave numbers shown in table.1

Table-1 FTIR frequencies of fundamental vibrations of pure KDP and doped samples.

Sr. No.	Pure KDP (cm $^{-1}$)	0.6% LV +KDP (cm $^{-1}$)	0.8% LV +KDP (cm $^{-1}$)	1.0% LV +KDP (cm $^{-1}$)	2.0% LV +KDP (cm $^{-1}$)	Assignment
1	3605	---	----	---	3572.41	Free O-H stretching Hydrogen bonded of KDP
2	3341	----	3472.45	--	3454.46	O-H-O stretching of NH_3^+ amino acid
4	2830	2836.73	2824.74	2820.74	2806.75	P-O-H symmetric stretching
5	2466	2464.90	2468.90	2468.90	2460	O=P-OH stretching
6	2362	2362.94	2362.94	2362	2366.89	NH_3^+ Bending superimposed with P-O-H bending of KDP

7	1655	1681.25	1671.25	1693.24	1635.27	O=P-OH stretching
8	1299	1301.42	1297.42	1299.42	1295.42	C-H bonding of LV
9	1101	1103.50	1097.51	1097.51	1099.51	P=O stretching
10	904	899.72	899.72	899.72	899.72	P-O-H stretching representing functional group of KDP
11	539	533.76	537.76	535.76	531.76	Symmetric HO-P-OH bending
12	416	411.81	397.82	409.81	405.81	PO_4 stretching

3.3 DTA and TGA analysis: TGA /DTA are powerful to investigate the melting behavior, Glass Transition, Crystallization, Oxidation Stability, Kinetics, Purity, and Specific Heat. DTA and TGA of KDP were carried out with the help of an instrument (STA 409C) using KDP crystals as sample and alumina as reference. LV doped KDP sample was decomposed at 272.20℃. The graphs show the peaks at 435.85 ℃ and 520℃ reveal exothermic reaction due to escape of oxygen atoms from the KDP crystal. TGA curve sharply decrease at temperature at 214 ℃ and 350℃ is most probable melting point of KDP crystal. TGA curve shows that crystals are thermally stable below 220 ℃. This shows that the presence of l-valine appears to increase the decomposition temperature of KDP. Fig. 5_a and 5_b shows TGA and DTA curves for LV doped KDP crystal. The DTA curve shows an endothermic peak at 272.20 ^{0}C, 435.85 ^{0}C, 520.5 ^{0}C. Enthalpy ΔHchanges in the endothermic reaction are 241.44 J/gm, 63.75 J/gm.

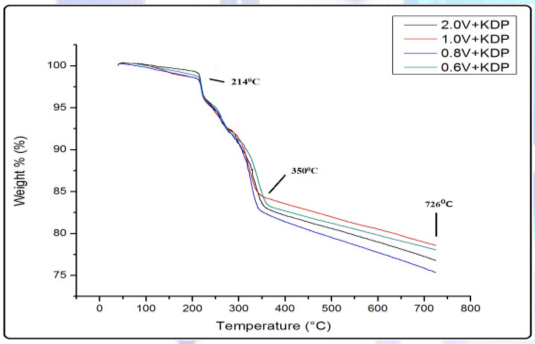

Figure 5_a. TGA curves of LV doped KDP

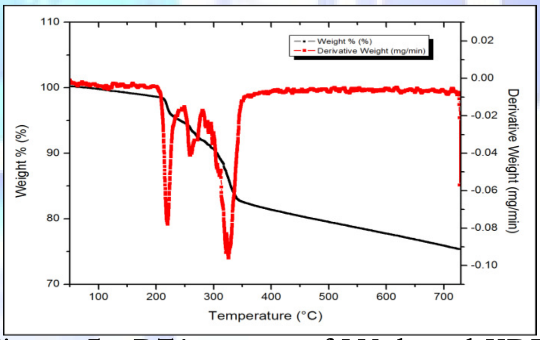

Figure 5_b. DTA curves of LV doped KDP

3.4 Microhardness test: The mechanical property of the materials is useful for determination for device fabrication [13] and it is directly related to its bonding and crystallographic orientation[14] Vickers indentation test studied on cut polished plate of (100) plane of thickness 5 mm in size shown in figure()with load (10gm,25gm,50gm & 100gm)using Vickers hardness tester with diamond indenter attached to an incident light microscope and the indentation time was kept as 10 sec for all loads. N. Karthick *et. al* reported the formula for calculation of Vicker's microhardness number *Hv*. Table-2 shows the Vickers hardness (Hv) for load used for the 1.0mole% and 2.0 mole% of LV doped KDP grown crystals. At 50 g the Hv of doped KDP was found 120.4 Hv and 122.0 Hv. This shows that the concentration of dopant increases the hardness property of crystals.

Figure 6. cut / polished plate of (100) plane.

Table -2 Vickers hardness (Hv) for load

Sample	Micro hardness number	Load used
1.0 % LV+KDP	120.4 Hv	50 gms
2.0 % LV+KDP	122.0 Hv	50 gms

4. Discussion and Conclusion

The bulk large size crystal of L-valine doped KDP has been grown successfully with the dimension up to 50 mm in height by modifying the CTB in SR method. The concentration of dopant increases the percentage of transmission in the entire visible and IR region. FTIR confirms the presence of higher concentration organic additives in potassium dihydrogen phosphate (KDP). The addition of L-valine organic impurity appears to increase the thermal stability of KDP crystal. The higher concentration grown crystals have higher hardness value.

Reference

[1] P.N. Prasad, D.J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, Wiley-Interscience, New York, 1991

[2] D.S. Chemla, J. Zyss, Nonlinear Optical Properties of Organic Molecules and Crystals, Academic Press, New York, 1987.

[3] Dongli Xu, Dongfeng Xue, Journal of Crystal Growth 310, 2008, 1385.

[4] P. Rajesh, S. Sreedhar, K. Boopathi, S.Venugopal Rao, P. Ramasamy 212-4, 2011, 1567

[5] A.J. Nelson, T. van Buuren, E. Miller, T.A. Land, C. Bostedt, N. Franco, P.K. Whit- man, P.A. Baisden, L.J. Terminello, T.A. Callcott, J. Electr. Spectr. 114 (2001) 873

[6] L. Misoguti, A.T. Varela, F.D. Nunes, V.S. Bagnato, F.E.A. Melo, J. Mendes Filho, S.C. Zilio, Opt. Mater. 6 (1996) 147.

[7] C. Razzetti, M. Ardoino, L. Zanotti, M. Zha, C. Paorici, Cryst. Res. Technol. 37 (2002) 456.

[8] P. Kumaresan, S. Moorthy Babu, P.M. Anbarasan, Optical Materials 30 (2008) 1361–1368.

[9] S. Balamurugan, P. Ramasamy, S.K. Sharma, Yutthapong Inkong, Prapun Manyum Materials Chemistry and Physics 117 (2009) 465–470

[10] O. V. Mary Sheeja, C. K. Mahadevan , Int. Journal of Engineering Research and Applications,4, (2014)55-65.

[11] N. pattanaboonmee, P. Ramasamy, P. Manyaum, , ferroelectric, 413, 2011, 96-107

[12] B Suresh Kumar & K Rajendra Babu, I. J. Pure & Applied Physics, 46, 2008, 123-126

[13] S. Balamurugan, P. Ramasamy, Materials Chemistry and Physics 112 (2008) 1–4

[14] N. Karthick ,R. Sankar, R. Jayavel , S. Pandi, J. of Crystal Growth 312 (2009) 114–119