Growth and Characterizations of KDP Single Crystal by Double Wall Sankarnarayan-Ramasamy Method

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Abstract
Potassium Dihydrogen Phosphate (KDP) are nonlinear optical materials and have been used as optical modulation and frequency converters. KDP single crystals have grown by Sankarnarayan–Ramasamy method. Powder X-ray diffraction studies revels that KDP crystal belongs to tetragonal structure with $I\bar{4}2d$ space group. The functional group has been determined by FT-IR spectral studies. The cut-off wavelength and optical transparency of the grown single crystals were observed using a UV–Vis spectrophotometer. Thermal and physio–chemical stability of the grown crystal were examined by TGA, DTA and DSC studies. The second harmonic generation SHG investigated of the grown crystal by the Kurtz powder technique. Dielectric property with frequency was investigated by of the grown KDP crystal.

Keywords: - Potassium Dihydrogen Phosphate (KDP), Sankarnarayan–Ramasamy method, XRD, FTIR, UV-NIR-VIS, SHG.

1. Introduction

Optical crystals with a high degree of perfection find applications in critical technology areas such as High- power lasers, higher harmonic generation and in the field of nuclear fusion. Frequency conversion is an important technique for extending the useful wavelength range of lasers. In photonics, a growing need continues for low cost, highly nonlinear, efficient and high quality crystals for optical frequency conversion. Nonlinear optical (NLO) organic materials have received much importance for optical second harmonic generation (SHG) owing to their practical applications in the domain of optoelectronics and photonics [1].

In the past decades, many efforts have been made to promote the crystal quality and increase the growth rate to meet the requirements of inertial confinement fusion. In recent years, various growth methods and apparatus have been continuously developed to improvement in quality and growth rate. The newly develop technology have been prefer to first applied on KDP crystal. The above said methods yield only small size single crystals. For certain applications like phase matching, where the specimen should have

more size along a particular direction, the crystals grown by these methods cannot serve the purpose [2,3].

The recently invented Sankaranarayanan– Ramasamy (SR) method has given the solution and it is possible to grow bulk size single crystals along a desired orientation needed. Aim of improving the quality of KDP crystals with better optical properties, an attempt has been made in the present work to grow the KDP crystals and to study the effect on the nucleation parameters and structural and optical properties [4-7].

2. Experimental

S-R method is unidirectional crystal growth method from solution as shown in fig1. Arrangement of coil and ampoule was placed inside the double wall cylindrical column to achieve errorless temperature gradient. Temperature gradient and evaporation rate are primarily parameter crystal growth in S-R method. This arrangement is improving growth rate and quality of single crystal. Seed crystals were prepared by convectional recrystallization slow evaporation method. KDP of Merck AR grade was used to prepared seed crystal. Very good and transparent qualities of seed crystals were selected having perfect external morphology. <100> crystal plane is selected for unidirectional growth in S-R method. Seed crystal was cut carefully and polished portion along <100> plane. The processed seed crystal was placed at the bottom of ampoule, which is special designed for S-R method [8,9].

Fig. 1: S-R Crystal growth setup and growth .

Solution was prepared at 30 ℃ according to solubility curve. Weight percentage of amount of Gallium nitrate was calculated for different concentration and dissolved in (Millipore 18.2 MΩ. cm resistance) triple filter deionized water. Amount of KDP solute Merck AR grade was dissolved in prepared solution. Solution was kept three hours on magnetic stirrer at 30 ℃ temperatures for homogeneity in the solution. Solution was kept slightly under saturated for S-R method. The solution filtered by whatman filter paper pore size 11. Clean filtered solution was carefully filled in ampoule without disturbing the position of seed crystal inside the ampoule.

The ampoule was rested in S-R set up for two hour. Initially, temperatures are kept 30 ℃ at upper and lower ring heater. The solution was settled

inside the ampule and concentration gradient maintain along the ampule. Concentration gradient was maintained minimum at top and maximum at the bottom of the ampoule. Upper ring heater temperature slightly is increased 35 °C for rising evaporation rate at top of the ampoule. The top ring heater controls the spontaneous nucleation near the surface region of the solution during crystal growth process. Upper part of ampoule was covered with transparency sheet and the small hole at the center is reduced nucleation at upper part of ampoule. A transparent KDP crystal growth was observed at the bottom of ampoule under optimizing condition in week. The KDP growth rate was approximately 1 mm per day is observed. A good transparent quality of crystal was harvested [10-14].

3. Characterization

The KDP crystal, which was developed by double wall SR-method, was studied rigorously by using X-ray diffraction analysis (XRD), Fourier transformation infrared spectroscopy (FTIR), Thermogravimetric analysis / Differential thermal analysis (TGA/DTA), Ultraviolet-visible (UV-visible) analysis, Second Harmonic Generation and Dielectric measurements.

3.1 powder crystal XRD: KDP crystal belongs to the tetragonal scalerohedral symmetry with space group $I\bar{4}2d$ having dimensions a = b = 7.4528Å and c = 6.9752Å. The sample was scanned in the range 10-90° at a scan rate 2° per min .The finely powered materials of the grown crystal were used for the analysis .The powdered diffraction pattern with indices are shown in figure 2. The prominent well resolved Bragg's picks of specific 2θ angle reveals the high crystalline nature of the crystal. The XRD data is verified by KDP crystal *JCPDS* Card nos. 35- 0807[15].

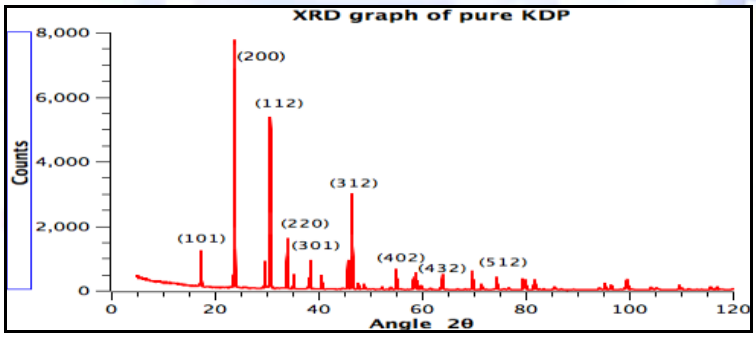

Fig 2. Powder XRD of KDP crystal

3.2 UV-VIS-IR Spectrum analyses: The UV-Vis-NIR spectral transmittance was studied using a Shimadzu UV-1061 UV-Vis spectrophotometer with a single crystal of 6 mm thickness in the range of 200-1200 nm. The recorded spectrum is shown in figure. The crystal has sufficient transmission in the entire visible and IR region. The lower cut off wavelength is around 250 nm; the transmission percentage of KDP crystal is around 93%, as compared to pure KDP, which is around 87% as shown in fig 3 [16].

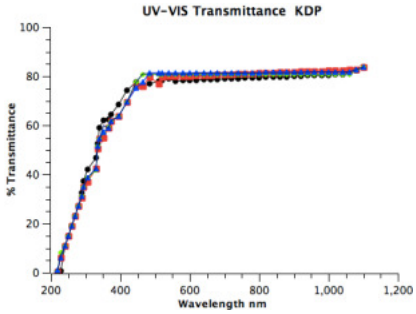

Fig 3. UV-VIS-IR spectrum

3.2 FTIR Spectrum analyses: Recording the spectrum using Varian FTIR spectrometer by ATR technique in order to reveal the metal complex coordination carried out the Fourier transform infrared analysis of powered sample. The obtained result testifies that all the IR spectra are practically identical and agree with the available literature data. The assignments confirm the presence of various functional groups present in the material. The wave number 3065,3334 cm $^{-1}$is presence of O-H bond, 2919, 2839, 2461 cm^{-1} presence of P-O-H bonding, 2358 cm $^{-1}$ represent P-O=H bond, 1295,1100 cm $^{-1}$ presence of P=O bond , 904 and 543 cm $^{-1}$ is represent of P-O-H bond as shown in fig 4 [17,18] .

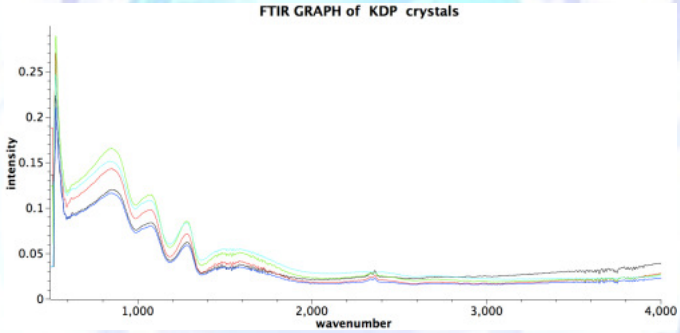

Fig 4. FTIR SPECTRUM

3.3 Frequency and Dielectric properties: Dielectric studies of the grown KDP crystal have been carried out at with frequencies and . The behavior of the crystal under electric field has close relationship with the laser light irradiation, and hence the power dissipation factor can be studied from the dielectric studies. The KDP crystal sample was coated with electrode on either side with silver paste to form a parallel plate capacitor. The dielectric constant (ε') and dielectric loss (ε'') were calculated from the equation

$$\varepsilon' = \frac{C\,t}{\varepsilon_0 A} \qquad \text{and} \qquad \varepsilon'' = \varepsilon' D$$

Where ε_0 is the permittivity of free space, t is the thickness of the sample, D is dissipation factor and A is the area of cross section of the sample.

The sample of size 5 mm diameter plate was used for dielectric studies. The dielectric constant and dielectric loss vs. frequency are plotted in Figs 5. The dielectric constant as a function of both frequency and resistance was

measured and the dielectric constant decreases with the increase in frequency and temperature [19-24].

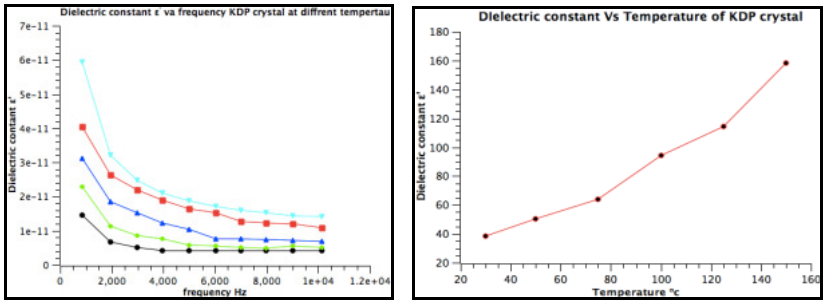

Fig 5. Dielectric properties with frequency and temperature

3.4 SHG Studies: To study the NLO property, powdered sample of KDP crystal was irradiated with the fundamental beam of 1064nm from Q-switched Nd:YAG laser. Pulse energy of 5.3 mJ/pulse, pulse width of 10ns and repetition rate of 10Hz was used to test the SHG. Emission of green light 532 nm from the grown crystal confirms the NLO property. The output power from the KDP crystal was compared to calibrated KDP crystal [25,26].

4. Conclusions

In this investigation, KDP single crystals were grown by the slow evaporation method in an aqueous solution and double wall S-R method. Crystalline nature and lattice parameter values of the KDP crystal were confirmed by powder X-ray diffraction analysis. The presences of functional groups were confirmed by FT-IR spectral analysis. Optical absorption of KDP single crystal was studied and it is observed that there is no absorption in the entire UV–visible region. SHG of the grown crystal was confirmed by the Kurtz powder technique and the emission of intense green light of the KDP crystal. Thermal stability and physiochemical changes of the grown KDP crystals were studied by TGA, DTA and DSC analyses and it is thermally stable up to 299 C against thermal energy .The dielectric studies reveal that KDP possesses low dielectric constant and low dielectric loss and hence it will be a promising material for electro-optic applications.

5. Reference

1. Eremina, T. A., Kuznetsov, V. A., Eremin, N. N., & Okhrimenko, T. M. (2005)., *273*, 586–593. doi:10.1016/j.jcrysgro.2004.09.068
2. Charoen-In, U., Ramasamy, P., & Manyum, P. (2010. *Journal of Crystal Growth*, *312*(16-17), 2369–2375. doi:10.1016/j.jcrysgro.2010.05.027
3. Supriya, S., & Kalainathan, S. (2011). Mechanical properties of β -Alanine doped Glycine phosphite single crystal grown by SR Method, *3*(3), 1373–1379.
4. Arunkumar, a., & Ramasamy, P. (2013), *1*, 1–5. doi:10.1016/j.jcrysgro.2013.10.049

5. Dinakaran, S., & Jerome Das, S. (2008). *Journal* Senthil Pandian, M., Boopathi, K., Ramasamy, P., & Bhagavannarayana, G. (2012). *Materials Research Bulletin*, *47*(3), 826–835. doi:10.1016/j.materresbull.2011.11.052
6. *of Crystal Growth*, *310*(2), 410–413. doi:10.1016/j.jcrysgro.2007.10.035
7. Nagaraju, D., Raja Shekar, P. V., Bhaskar Rao, T., & Kishan Rao, K. (2010). *Materials Letters*, *64*(3), 267–270. doi:10.1016/j.matlet.2009.10.059
8. Senthil Murugan, G., Perumal Ramasamy, R., Ramasamy, P., & Bhagavannarayana, G. (2011). *Journal of Crystal Growth*, *328*(1), 58–61. doi:10.1016/j.jcrysgro.2011.06.026
9. Rameshkumar, P., Gunaseelan, R., Kumararaman, S., Baghavannarayana, G., & Sagayaraj, P. (2011*Physica B: Condensed Matter*, *406*(6-7), 1204–1210. doi:10.1016/j.physb.2010.11.033
10. Rajesh, P., Ramasamy, P., Bhagavannarayana, G., Kumar, B., Growth, C., & College, S. S. N.
11. Reddy, J. N. B., Vanishri, S., Kamath, G., Elizabeth, S., Bhat, H. L., Isakov, D., … Aroso, T. L. (2009*Journal of Crystal Growth*, *311*(16), 4044–4049. doi:10.1016/j.jcrysgro.2009.06.041
12. doi:10.1016/j.matchemphys.2009.06.011
13. Rajesh, P., & Ramasamy, P. (2009). *Spectrochimica Acta. Part A, Molecular and Biomolecular Spectroscopy*, *74*(1), 210–3. doi:10.1016/j.saa.2009.06.024
14. N. P. Rajesh, V. Kannan, P. SanthanaRaghavan, P. Ramasamy, and C. W. Lan, *Materials Chemistry and Physics*, vol. 76, no. 2, pp. 181–186, 2002.
15. N.P. Rajesh, V. Kannan, M. Ashok, K. Sivaji, P. SanthanaRagavan, P. Ramasamy,
16. N. Balamurugan, P. Ramasamy, Cryst. Growth Design 6 (2006) 1642.
17. Christer B. Aakeroy, Peter B. Hitchcock, J. Mater. Chem. 3 (11) (1993) 1129.
18. A.A. Chernov, L.N. Rashkovich, A.A. Mkrtchan, Sov. Phys.-Cryst. 32 (1987) 432.
19. L.N. Rashkovich, G.T. Moldazhanova, Crystallogr. Rep. 39 (1994) 135.
20. A.A. Chernov, in: A.V. Shubnikov, N.N. Sheftal (Eds.), Growth of Crystals, vol. 3, Consultants Bureau, New York, 1962, p. 35.
21. C. N. Banwell and E. M. McCash, *Fundamentals of Molecular Spectroscopy*, McGraw-Hill, New York, NY, USA, 4th edition, 1994..
22. J. F. Bringly, M Rajeshwaran, Acta.Cryst.,E62, m1304 (2006).
23. N. Vijayan, N. Balamurugan, R. Rameshbabu, R. Gopalakrishnan, P. Ramasamy, W.T.A. HarrisonJ. CrystalGrowth 267 (2004) 218.
24. N.V. Prasad, G. Prasad, T. Bhimasankaran, S.V. Suryanarayana, G.S. Kumar, Indian J. Pure Appl. Phys. 14
    a. (5) (1969) 639.
25. V. Krishnakumar and R. J. Xavier, *SpectrochimicaActa Part A*, vol. 61, no. 8, pp. 1799– 1809, 2005.
26. Wang yaoshui, P. Bennema,W.H. Van der linden, J. Boshaar, J.W.M. Van kessel,H. Clapper, J. Crystal Growth 83 (1987) 471.