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Effect of Pd^{2+} Doped on the Growth, Optical, Mechanical and Dielectric Properties of KAP Single Crystal

Viji niraimathi[1,*], V. Aroulmoji[2], G. Rajarajan[2]

[1]Department of Physics, Dhirajlal Gandhi College of Technology, Salem, Tamilnadu, India
[2]Centre for Research and Development, Mahendra Educational Institutions, Tiruchengode, Tamilnadu, India
*Corresponding author: vijiniraimathi@yahoo.com

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Abstract In the present investigation, we have successfully grown optically transparent single crystals from aqueous solution by slow evaporation technique. The influence of dopant Pd^{2+} on the growth process, crystalline properties of potassium acid phthalate (KAP) has been investigated. Powder XRD and ICP-OES studies confirmed the Pd^{2+} ion doping into KAP crystals. The modes of vibration in the crystal lattice have been determined by FTIR analysis. Optical transmission studies were carried out by allowing the UV-NIR ray of wavelength between 190 and 1000 nm, which is to pass through the (010) face of the grown KAP crystals and the results confirm that both the pure and doped KAP single crystal shows good transparency in the entire visible region, which is suitable for optical device applications. TGA studies reveal that the purity of the sample and no decomposition is observed below the melting point. Microhardness studies reveal that the Pd^{2+} doped crystals have higher hardness values than that of pristine KAP. Dielectric constant value of Pd^{2+} doped KAP at 100 Hz was found to be extensively higher than that of pristine KAP. The Pd doping significantly improves the second harmonic generation (SHG) efficiency of the KAP host crystal.

Keywords: *single crystal, solution growth, Pd^{2+} ion doping, dielectric properties, thermal analysis, nonlinear optical materials*

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1. Introduction

Second order nonlinear optical (SONLO) materials have recently attracted much attention because of their potential applications in emerging optoelectronic technologies. It has been reported that organic crystals have very large nonlinear susceptibility compared with inorganic crystals, but their use is impeded by low optical transparency, poor mechanical strength, low laser damage threshold and inability to produce and process large crystals [1]. Potassium Hydrogen Phthalate (KHP) crystal, with the chemical formula $[K(C_6H_4COOH\text{-}COO)]$, is well known for its application in the production of crystal analyzers for long-wave X-ray spectrometers. Also, Potassium Hydrogen Phthalates have piezoelectric, pyroelectric, elastic and non-linear optical properties [2]. KAP belongs to the series of alkali acid phthalates which crystallizes in the orthorhombic structure. The crystals have excellent physical properties and have a good record for long term stability in devices KAP crystals are also used as the second, third and fourth harmonic generators for Nd:YAG and Nd:YLF lasers. Recently, KHP crystals are used as substrates for the growth of highly oriented film of conjugated polymers with nonlinear optical susceptibility [3]. KAP single crystals have been grown from solvent evaporation technique [4], floating seed technique [5] and slow cooling technique [6]. Recently a slow evaporation technique for the growth of KAP single crystals from solution has been developed [7]. The slow evaporation method is suitable to grow bigger size KAP crystals. Moreover, the simple, effective, and low-cost route to synthesis process shows a good application prospect for second harmonic generation. The addition of some transition metal ions is expected to influence the growth kinetics, habit modification and the large size single crystal. The metallic ion dopants (Fe^{3+}, Cr^{3+}, Zn^{2+}, Mg^{2+}, etc.) in the KAP crystals are reported to induce significant changes in optical, ferroelectric and nonlinear optical behaviors [8]. Kejalakshmy and Srinivasan [6] have reported that the metal ion (Cr and Fe) doped KAP crystals serve as good electro-optic modulator. Parthiban et al. [9] also reported that the Zn^{2+} doping into KAP crystals improves the optical properties and its SHG efficiency. The aim of the present work is to grow optically transparent, good quality KAP crystal by doping different concentrations of Pd^{2+} ions and to explain the influence of Pd^{2+} ions on thermal, structural, optical, and dielectric behaviour of pure KAP. To the best of our knowledge this is the first preliminary report about thermal, structural, optical and dielectric properties of Pd doped KAP single crystal.

2. Experimental Procedure

Potassium Acid Phthalate (KAP) crystals were grown by the slow evaporation solution growth technique at room temperature with double distilled water as solvent. A recrystallization process was carried out in order to eliminate impurities in the KAP crystal. Initially saturated KAP solution was prepared at room temperature and filtered using microfilter paper of 0.1 µm. The divalent impurity of Pd^{2+} ions were selected as dopant in the form of $PdCl_2$. $PdCl_2$ concentration in the solution was varied from 0.1 to 0.3 mol%. The prepared saturated solutions of pure and Pd^{2+} doped KAP were well stirred and stored in separate beakers covered with perforated sheets. The pH values of all the solutions were found to be 4. The solution was filtered with a microfilter. The seed crystals are allowed to float on the surface of the saturated solution and left for slow evaporation at room temperature (30°C). The crystals were formed by evaporation of solvent with time interval of 4 days. The grown crystals were harvested and subjected to characterization studies. The pH values of the final solutions after harvesting the crystals were found to be 4.0 as that of initial solution.

2.1. Characterization Details

Powder X-ray diffraction pattern of all the grown crystals were recorded on Joel JDX 8030 diffractometer (CuKα1 wavelength 1.5406 Å). Thermogravimetric analysis was carried out between 30° and 1000°C in air atmosphere using Universal V4.3A TA instrument (SDT Q600 V8.3 Build 101) with the heating rate of 20 °C/min. Elemental analyses were made by using Perkin Elmer optima 5300 DV ICP-OES instrument. UV-NIR spectrum was recorded on a Perkin Elmer Lambda 25 spectrometer in transmission mode. FTIR transmittance spectra of pristine and doped KAP crystals were recorded in the range of 400 - 4000 cm^{-1} using Lamda 35 make Perkin Elmer (Spectrum RX1) spectrometer. Dielectric studies were carried out on (010) faces of the grown crystals using Hioki 3532-50 LCR Hitester. Microhardness measurements were carried out using Shimadzu tester. Second harmonic generation (SHG) of the samples was measured by Kurtz powder method. A Q switched Nd:YAG laser beam of wavelength 1064 nm was used within an input energy of 5.02 mJ/pulse and the pulse width of 8 ns, the depletion rate being 10 Hz. The SHG radiation of 532 nm (green light) emitted were collected by a photo multiplier tube (PMT-Philips Photonics model 8563) and the optical signal incident on the PMT was converted into voltage output at the CRO (Tektonic-TDS 3052).

3. Results and Discussion

3.1. Crystal Growth

The pure and Pd doped KAP single crystals were shown in Figure 1. There has been no significant change in the color and crystal morphology due to magnesium doping. Inductively coupled plasma-optical emission spectrometric (ICP-OES) analysis confirmed the presence of dopants in the order of 13.25, 15.14, 17.15 mg/L for Pd (0.1, 0.2 & 0.3 mol %) doped KAP respectively. These cations may be placed in between the two adjacent layer of the KAP or may be substituted only for potassium ion without disturbing the carboxylic acid group.

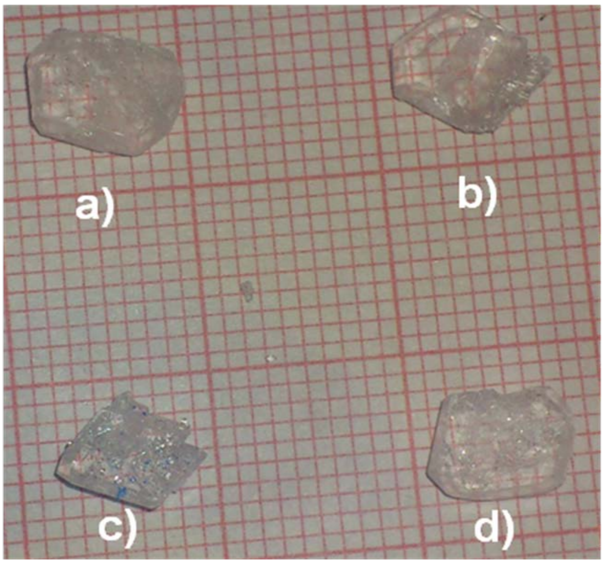

Figure 1. Photographs of as grown KAP crystals; (a) pure, (b) 0.1 mol% Pd, (c) 0.2 mol% Pd, (d) 0.3 mol% Pd

The pH value of the mixed solution remained unchanged throughout the growth run similar to that of pure KAP solution. The pH of the solution depends on the concentration of H^+ ions present in the solution. Here, it is possible that the dopant Pd^{2+} ions substitute for K^+ ion or it may get into the interstitial sites without disturbing the carboxylate hydrogen of the compound in the solution.

3.2. Powder XRD Analysis

The XRD pattern of pure and Pd doped KAP single crystals were shown in Figure 2. The results confirmed that both the pure and Pd doped KAP single crystals grew in orthorhombic structure with space group $Pca2_1$, which is in good agreement with the standard JCPDS data (31-1855). It can be noted that the clear peak shift was observed for the Cu doped crystals when compared to the undoped KAP. These shifts in peak positions caused a change in lattice parameters when compared to the pure KAP. The peak intensity also decreases with increase of Pd content. The lattice parameters were calculated from the equation for the orthorhombic crystal system using the method of least squares.

$$\lambda = 2d_{hkl} \sin \theta_{hkl}$$

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \text{ and volume } V = abc$$

Where d is the lattice spacing, and (h, k, l) is the Miller indices, a, b and c are the lattice parameters, λ is the wavelength and 2θ is the diffraction angle. The cell parameters and volume of pure and doped KAP crystals were calculated and the values are in good agreement with the reported values [10]. There is a slight change in the lattice parameter and volume of the doped crystals. This may be due to the lattice distortion by doping in the parent compound. It should be remembered that ionic radii of Pd (88 Å**)** is very small compared with that of K (1.52 Å).

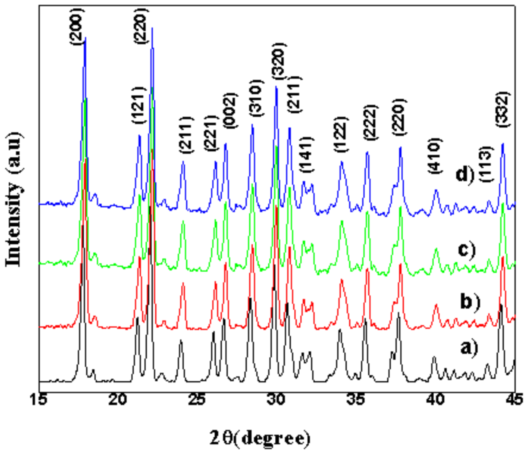

Figure 2. Powder XRD patterns of KAP crystals; (a) pure, (b) 0.1 mol% Pd, (c) 0.2 mol% Pd, (d) 0.3 mol% Pd

Table 1. Lattice parameters of pure and Pd^{2+}ion doped KAP crystals

Lattice Parameters	Pure KAP	0.1 mol% PD	0.2 mol% PD	0.3 mol% PD
a (Å)	96S7	9 65S	9.654	9.654
b(Å)	13310	132J8	13.355	1342S
c(Å)	6.479	6435	6 475	6482
Volume(Å)^3	835.815	824.301	833.621	841.202

3.3. Thermal Analysis

In order to identify the thermal stability, purity and crystalline nature of solution grown pure and Pd doped KAP crystals, they were subjected to thermal analysis. The TG-DTA curves of pure and Pd (0.3 mol %) doped KAP crystals were shown in Figure 3 & 4 respectively. Experimentally observed weight loss at various stages of decomposition agrees well with the theoretically calculated values according to the following equations [11]:

$$2KC_8H_5O_4 \rightarrow K_2C_8H_5O_4 + C_7H_5O_2 + CO_2 \tag{1}$$

$$K_2C_8H_5O_4 \rightarrow K_2CO_3 + C_7H_5O \tag{2}$$

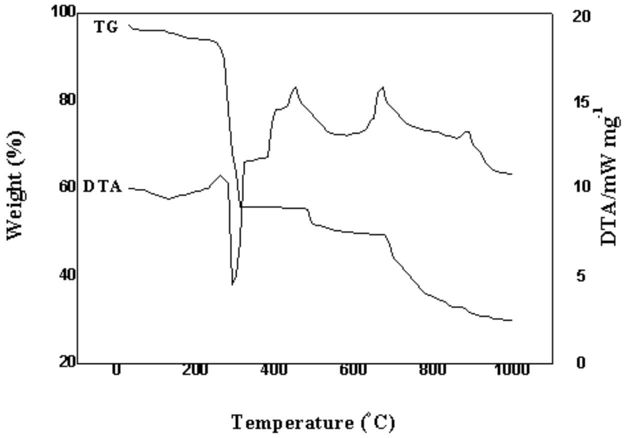

Figure 3. TG-DTA analyses of pure KAP crystals

The thermal analysis shows that there is no physically adsorbed water in the molecular structure of crystals grown from doped solution. Studies reveal that the purity of the materials. The weight loss starts at around 260°C and about 45% of the total weight loss has occurred during the initial decomposition of both pure and doped KAP according to Eq. (1).

The endothermic peak is obtained in DTA for Pd doped crystals at a little bit higher temperature (312°C) compared to the pure KAP crystals (303°C). The total weight loss up to 1000°C was found to be 82% and 84% for pure and Pd (0.3 mol%) doped KAP respectively. No decomposition below the melting point ensures the stability of the material for application in lasers where the crystals are required to withstand high temperatures. The significant changes in TG-DTA curves confirm that the Pd^{2+} ions were doped into the crystalline matrix.

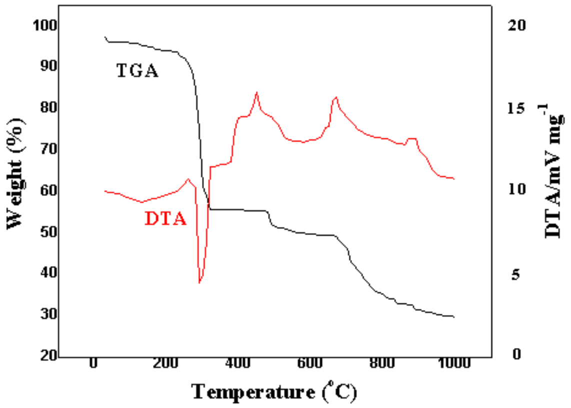

Figure 4. TG-DTA analyses of Pd (0.3 mol%) doped KAP crystals

3.4. Optical Transmittance Studies

The UV-VIS-NIR spectrum gives limited information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electron in π and σ orbital from the ground to higher energy states. A transmission spectrum is very important for any NLO material because a non linear optical material can be of practical use only if it has a wide transparency window [12]. The as grown crystals of higher quality with thicknesses of 2.1, 2, 2.2 and 2.3 mm for pure and Pd (0.1, 0.2 & 0.3 mol %) doped KAP respectively were placed in the crystal holder and the UV-NIR ray of wave length 190-1000 nm was allowed to pass through the (0 1 0) face of grown crystals (Figure 5). All the crystals have 35-55% transmittance crystals. From the graph, it is evident that both pristine and Pd doped KAP crystals have their UV cut off below 300 nm, which is sufficient for SHG laser radiation of 1064 nm or other application in the blue region. It is also observed that the transmittance found to increase in the presence of dopants. The observed increment of transmittance confirms the doping of divalent ion into KAP.

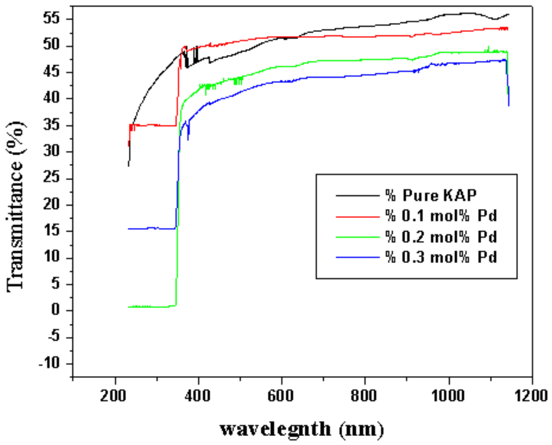

Figure 5. UV-NIR spectra of KAP crystals; (a) pure, (b) 0.1 mol% Pd, (c) 0.2 mol% Pd, (d) 0.3 mol% Pd

3.5. FTIR Analyses

Infra–red spectrum is an important record, which gives sufficient information about the structure of a compound. Fourier transform infrared spectra of pure and Pd doped KAP are shown in Figure 6. The observed vibrational frequencies and their assignments are listed in Table 2. Close observations reveal that a significant increase in peak intensity occurs at the –C=O carboxylic ion = O symmetric stretching vibration mode around 1390 cm^{-1} for metal ion doped KAP when compared to that of pure KAP. On the other hand, peak intensity corresponding to –C=O carboxylic ion=O symmetric stretching 1570 cm^{-1} remained almost unchanged for both pure and doped KAP [9]. The C=C ring stretching is present around 1486 cm^{-1} for both undoped and doped samples. C-H stretching vibration appears near 2471 cm^{-1} in all the investigated samples. The peak around 3452 cm^{-1} corresponding to O-H stretching hydrogen bond was found to be different significantly interms of intensity. In exacting, the peak intensity of 3458 cm^{-1} is very strong for Pd (0.3 mol %) doped KAP when compared to the peaks 3449 cm^{-1} and 3441 cm^{-1} for Pd (0.1 & 0.2 mol %) doped KAP respectively. The difference in sharpness of multiple bands in this region may also be taken as evidence for the doping of divalent metal ions

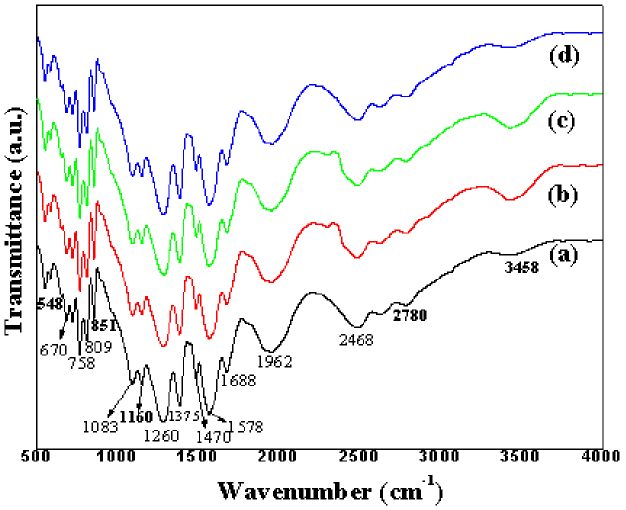

Figure 6. FTIR spectra of KAP crystals; (a) pure, (b) 0.1 mol% Pd, (c) 0.2 mol% Pd, (d) 0.3 mol% Pd

Table 2. Vibrational assignments of pure and Pd doped KAP single crystal

Pure KAP (cm^{-1})	0.1 mol% PD (cm^{-1})	0.2 mol% PD (cm^{-1})	0.3 mol% PD (cm^{-1})	Assignments
3455	3441	3449	3458	O-H stretching hydrogen bond
2478	2480	2482	2486	-C-H aromatic stretching
1952	1948	1946	1951	C=C asymmetric stretching
1678	1674	1671	1676	C=C stretching
1568	1561	1562	1558	-C=O carboxylic ion=O (A.S)
1480	1479	1474	1472	C=C ring stretching
1385	1386	1388	1384	-C=O carboxylic ion=O (S.S)
1270	1274	1276	1271	C-O stretching
1160	1161	1163	1166	C-C stretching
1083	1082	1085	1089	C-C=O stretching
851	854	853	852	C-H out of plane bending
754	756	757	754	C-C stretching
675	679	681	679	C-O Wagging
548	543	542	546	C=C-C out of plane ring deformation

3.6. Microhardness Studies

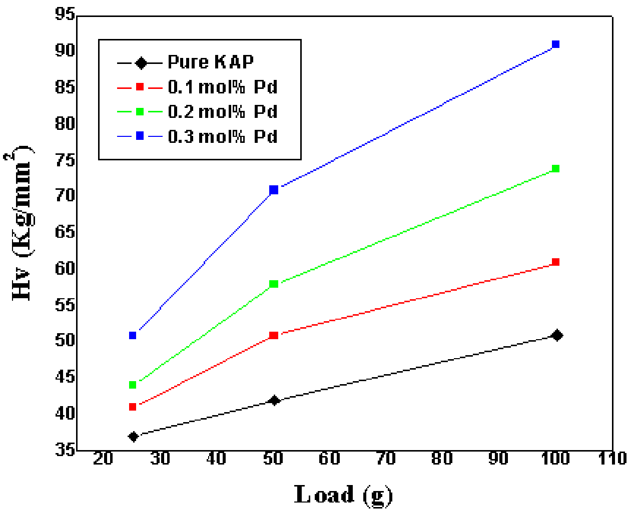

Figure 7. Vickers hardness vs. load of pure and Pd doped KAP crystals

Measurement of hardness is a useful nondestructive testing method to determine the hardness of the material [13]. Vickers microhardness test was carried out on pure and Pd doped KAP single crystals using microhardness tester flitted with a diamond indenter. The indentations were made using a Vickers pyramidal indenter for various loads from 25, 50 and 100 g. The microhardness values were calculated from the formula Hv = 1.8544 P/d^2 kg/mm^2, where Hv is the Vickers microhardness number, P is the applied load (kg) and d is average diagonal length of the indentation (nm) [14]. The hardness values as a function of load shown are shown in Figure 7. The result depiction that the microhardness values are higher for 0.3 mol % Pd doped crystal than compared to pristine KAP crystal. In contrary Hv value was decreased for 0.1 mol % Pd doped crystal decreased when compare to pure KAP crystal. The results suggest that 0.3 mol % Pd doped crystals are preferred for device fabrication than the undoped and 0.1 mol % Pd doped KAP crystals.

3.7. Dielectric Measurements

A sample with graphite coating on two opposite faces was placed between two copper electrodes and thus a parallel plate capacitor was formed. The capacitance of the sample was measured at various frequencies ranging from 100 Hz to 5 MHz. Dielectric constant (ε_r) and dielectric loss ($\tan\delta$) were calculated using the relation $\varepsilon_r = Cd/\varepsilon_0 A$ and $\tan\delta = D\varepsilon$, where C is the capacitance, d is the thickness of the crystal, A is the area of cross-section and ε_0 is the dielectric permittivity of vacuum (8.854 x 10^{-12}

F/m) [15]. The dielectric constant and dielectric loss for pure and Pd ion doped KAP crystals measured at 40°C are shown in figs. 8 and 9 respectively. From the graphs, it is clearly seen that dielectric constant (ε_r) decreases as the frequency increases in all cases. The higher values of dielectric constant at low frequencies may be due to the presence of all the four polarizations namely space charge, oriental, electronic and ionic polarization and its low values at high frequencies might be due to the loss of importance of these polarizations [16].

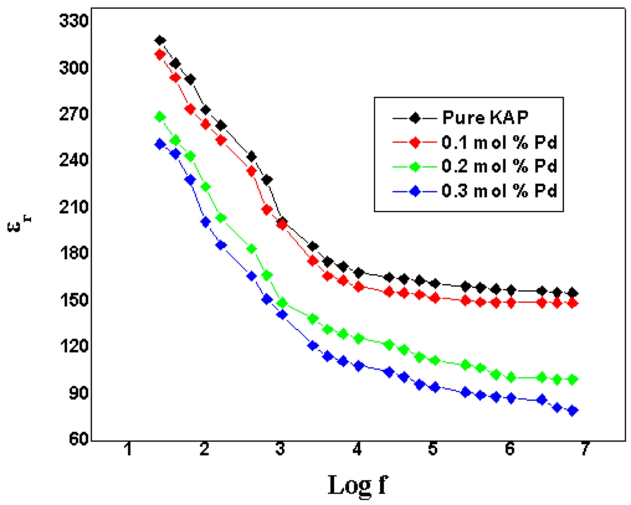

Figure 8. Dielectric constant vs log frequency measured at 40 °C of pure and Pd doped KAPcrystals

The dielectric constant (ε_r) values were estimated as 251, 263, 320 and 335 for pure and Pd (0.1, 0.2 & 0.3 mol %) doped KAP respectively. The dielectric constant of 0.3 mol % Pd doped KAP is much higher when compared to that pure and 0.1 & 0.2 mol % Pd doped KAP crystal. The dielectric loss of pure and Pd doped KAP crystals were shown in Figure 9. It clearly shows the dielectric loss (tanδ) value of 0.3 mol % doped KAP crystal has much lower when compare to pure and 0.1 & 0.2 mol % Pd doped KAP crystal. In both pure and doped crystals, dielectric loss decreases with increase in the frequency. This suggests that the dielectric loss is strongly dependent on the frequency of the applied field and very low dielectric loss indicates the high purity of the crystals.

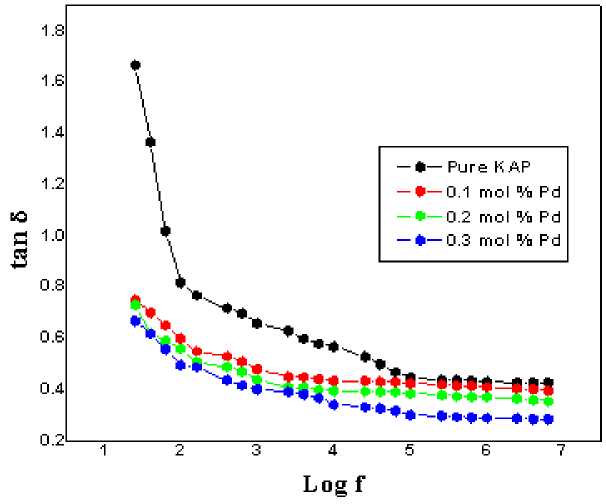

Figure 9. Dielectric loss vs log frequency measured at 40 °C of pure and Pd doped KAP crystals

3.8. SHG measurements

In order to confirm the NLO property of the grown crystals, they were characterized with a Nd:YAG laser with the wavelength of about 1064 nm. This high intense beam was allowed to be incident on the powdered sample. The emission of green light confirmed the second harmonic generation properties of the crystal.

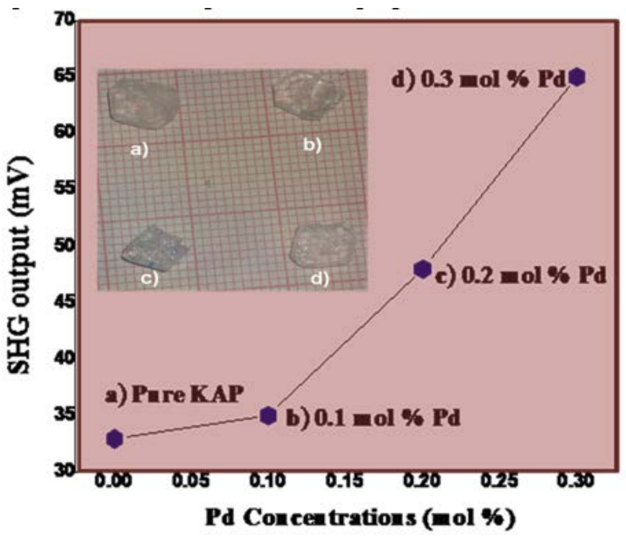

Figure 10. Shows the SHG efficiency of pure and Pd doped KAP crystals

The input beam energy was 5.02 mJ/pulse and pulse width of 8 ns, the repetition rate being 10 Hz. The SHG radiations of 532 nm (green light) emitted were collected by a photo multiplier tube (PMT-Philips Photonics model 8563) and the optical signal incident on the PMT was converted into voltage output at the CRO (Tektronix-TDS 3052). Figure 10 shows the SHG efficiency of pure and Pd doped KAP crystals. The SHG efficiency of pure KAP crystal was found to be 33 whereas the Pd (0.1, 0.2 & 0.3 mol %) doped KAP crystals were estimated as 35, 48, 65 mV respectively. For KDP it was 31 mV. Hence the SHG efficiency for 0.3 mol % Pd doped crystal was 2.09 times that of the KDP crystal. Hence the 0.3 mol % Pd doped crystals are suitable for device fabrication in NLO technologies than the pure KAP.

4. Conclusions

In summary, we have successfully synthesized good optical quality single crystals of palladium (Pd) doped potassium acid phthalate (KAP) by slow evaporation technique at room temperature. Powder X-ray diffraction results confirmed that all the doped materials are crystallized in the orthorhombic structure. Elemental analysis by ICP-OES confirmed the Pd^{2+} ions doping into the grown KAP crystals. The FTIR spectrum confirmed the presence of functional groups in the pure and doped compounds. Optical transmittance studies revealed that the pure and doped KAP crystals have transmittance in the entire visible region, which is essential for optical device applications. TGA studies reveal that the purity of the sample and no decomposition is observed below the melting point. Microhardness studies reveal that the Pd^{2+} doped crystals have higher hardness values than that of pristine KAP. Dielectric constant value of Pd^{2+} doped KAP at 100 Hz was found to be extensively higher than that of pristine KAP. The values of the second harmonic generation efficiencies obtained by Kurtz powder method confirmed that the 0.3 mol % Pd doped crystals are suitable for device fabrication in nonlinear optical applications.

References

[1] Baraniraja, T., and Philominathan, P., Journal of Minerals & Materials Characterization & Engineering, 10 (9). 805. 2011.

[2] Miniewicz, A., and Bartkiewicz, S., Advanced Materials for Optics and Electronics, 2 (4) 157. July/August 1993.

[3] Mavrin, B.N., Koldaeva, M.V., Zakalyukin R.M, Turskaya, T.N. Opt. Spectrosc. 100. 862. 2006.

[4] Alex, A.V., Philip, J. J. Appl. Phys. 88. 2349. 2000.

[5] Kejalakshmy, N., and Srinivasan, K. J., Phys. D. Appl. Phys. 36. 1778. 2003.

[6] Srinivasan, K., Meera, K., Ramasamy, P. J. Cryst. Grow. 205. 407. 1999.

[7] Karnal, A. K, Saxeena, A., Bhat, H. L., Wadhawan, V. K., Nathan, T. P. S, J. Cryst. Grow. 289. 617. 2006.

[8] Elakkina Kumaran, A., Kanchana., P. Sekar C. Spectrochimica Acta Part A. 91. 370. 2012.

[9] Parthiban, S., Murali. S., Madhurambal. G., Meenakshisundaram., S. P, Mojumdar, S.C. J. Therm. Anal. Calorim. 100. 751. 2010.

[10] Kanchana, P., Elakkina Kumaran, A., Sekar C. Spectrochim. Acta, Part A. 112. 21.2013.

[11] Alessandri, I., Bontempi, E., Sangaletti, L. Pagliara, S., Malavasi, L., Parmigiani F, Phys IV France. 118. 165. 2004.

[12] Uthayarani, R., Sankar, C. K, Shashidharan Nair. Cryst. Res. Technol. 43. 733. 2008.

[13] Uthrakumar, R.., Vesta, C. Justin Raj C. Krishnan, S. Jerome Das, S. Curr. Appl. Phys. 10. 548. 2010.

[14] Parimaladevi, R., Sekar, C., Krishnakumar, V. Spectrochim. Acta, Part A. 75. 617. 2010.

[15] Parimaladevi, R.., Sekar, C., Spectrochim. Acta, Part A. 76. 490. 2010.

[16] Chithambaram, V., Jerome Das, S., Arivudai Nambi R., Srinivasan K., Krishnan, S., Physica B. 405. 2605. 2010.