

Influence of Mg^{2+} dopant on structural, optical and mechanical properties of potassium acid phthalate (KAP) single crystals

V. NIRAIMATHI^{a*}, V. AROULMOJI^b, P. M. ANBARASAN^c, G. RAJARAJAN^b

^aDepartment of Physics, Dhirajlal Gandhi College of Technology, Salem – 636 004, Tamilnadu, India

^bCentre for Research and Development, Mahendra Educational Institutions, Tiruchengode - 637 503, Tamilnadu, India

^cDepartment of Physics, Periyar University, Salem – 636 011, Tamilnadu, India

The influence of dopant Mg^{2+} on the growth process, crystalline properties of potassium acid phthalate (KAP) has been investigated. Optically transparent single crystals have been grown from aqueous solution by slow evaporation technique. Powder X-ray diffraction (XRD) and inductively coupled plasma-optical emission spectrometry (ICP-OES) studies confirmed the Mg^{2+} ion doping into KAP crystals. The modes of vibration in the crystal lattice have been determined by Fourier Transform Infrared (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. Thermogravimetric (TGA) studies reveal that the purity of the sample and no decomposition is observed below the melting point. Microhardness studies reveal that the Mg^{2+} doped crystals have higher hardness values than that of pristine KAP. Dielectric constant value of Mg^{2+} doped KAP at 100 Hz was found to be extensively higher than that of pristine KAP. The grown crystals were also subjected to second harmonic generation (SHG) efficiency tests.

(Received June 21, 2014; accepted January 21, 2015)

Keywords: Potassium acid phthalate, Solution growth, Mg^{2+} ion doping, Optical properties, Thermal analysis, SHG efficiency

1. Introduction

Semi-organic crystals have attracted considerable interest due to their large nonlinear optical coefficients, high resistance to laser induced damage, low angular sensitivity and excellent mechanical hardness. Potassium Hydrogen Phthalate (KHP) crystal, with the chemical formula $[K(C_6H_4COOH-COO)]$, 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 [1]. KAP belongs to the series of alkali acid phthalates which crystallizes in the orthorhombic structure. A semi organic compound of Potassium Hydrogen Phthalate crystallizes in an orthorhombic system with the space group of $Pca2_1$ and its lattice parameters are $a = 9.605 \text{ \AA}$, $b = 13.331 \text{ \AA}$, $c = 6.473 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$ [2]. It has platelet morphology with a perfect cleavage along the {010} plane. 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. The crystals are extensively used for electro-optical applications as Q-Switches for Nd:YAG, Nd:YLF, Ti:Sapphire and Alexandrite lasers, as well as for acousto-optical applications. KAP crystals are often used as substrates for the deposition of thin films of organic nonlinear optical materials [3]. The addition of some transition metal ions is expected to influence the growth kinetics, habit

modification and the large size single crystal. The presence of small amount of impurities such as Ni^{2+} , Mg^{2+} , Co^{2+} and Li^{2+} plays an important role in the growth rate, habit modification of the crystal and its optical, ferroelectric and nonlinear optical behaviors [4]. The growth kinetics and optical and mechanical properties of KHP crystals by the effect of deuteration have also been analyzed [5]. G. Vasuthevan [6] has investigated that Hg and Pb doped KAP single crystal by slow evaporation technique. They concluded that dopant materials can lead to more optical and SHG properties than undoped KAP. S. Parthiban [7] et. al has reported Zn doped KAP single crystal by slow evaporation method. They also observed the doping metal ion (Zn) to change the morphology and significantly improve the second harmonic efficiency (SHG) of the pure KAP single crystal. In an effort to further improve the NLO behavior, optical and mechanical property of KAP, we have investigated the effect of Mg^{2+} ion dopant on the growth, structural, thermal, dielectric, optical, second harmonic generation efficiency of the KAP crystals.

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 μ m. The divalent impurity of Mg²⁺ ions were selected as dopant in the form of MgCl₂. MgCl₂ concentration in the solution was varied from 0.1 to 0.3 mol%. The prepared saturated solutions of pure and Mg²⁺ doped KHP 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 (CuK α 1 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 Mg doped KAP single crystals were shown in Fig. 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 Mg (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. 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 Mg²⁺ ions substitute for K⁺ ion or it may get into the interstitial sites without disturbing the carboxylate hydrogen of the compound in the solution.

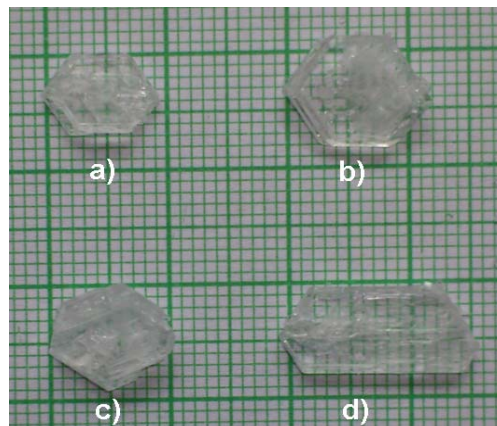


Fig. 1. Photographs of as grown KAP crystals; (a) pure, (b) 0.1 mol% Mg, (c) 0.2 mol% Mg, (d) 0.3 mol% Mg.

3.2 Powder XRD analysis

The XRD pattern of pure and Mg doped KAP single crystals were shown in Fig. 2. The results confirmed that both the pure and Mg doped KAP single crystals grew in orthorhombic structure with space group Pca2₁, which is in good agreement with the standard JCPDS data (31-1855). It can be seen that the clear peak shift was detected for the Mg 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 Mg content. The lattice parameters were calculated from the equation for the orthorhombic crystal system using the method of least squares.

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

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

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 results are listed in Table 1. There is a slight variation in the lattice parameters which could be attributed to the doping of divalent impurity ions at potassium site. Similar findings were observed for trivalent (Al³⁺, Cr³⁺ and Fe³⁺) ions doped KAP crystal [8].

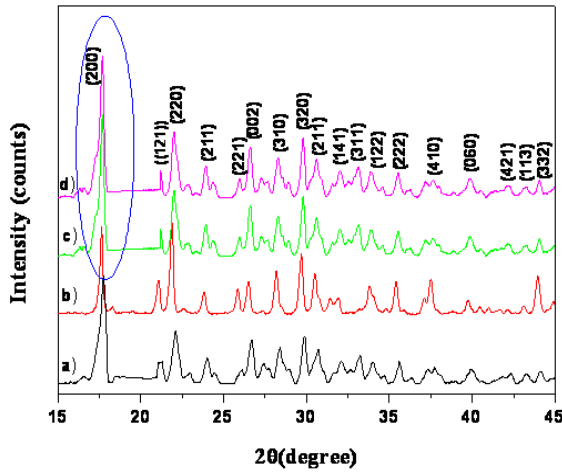


Fig. 2. Powder XRD patterns of KAP crystals; (a) pure, (b) 0.1 mol% Mg, (c) 0.2 mol% Mg, (d) 0.3 mol% Mg

Table 1. Lattice parameters of pure and Mg²⁺ ion doped KAP crystals

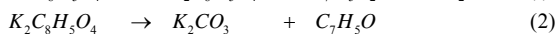
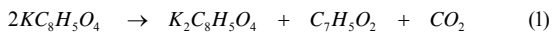
Lattice Parameters	Pure KAP	0.1 mol Mg	0.2 mol Mg	0.3 mol Mg
a (Å)	9.741	9.748	9.751	9.753
b (Å)	13.361	13.458	13.561	13.567
c (Å)	6.541	6.545	6.565	6.564
Volume (Å) ³	851.307	858.629	868.111	868.541

It should be remembered that ionic radii of K (1.52 Å) is higher than that of dopant ions Mg (0.86 Å). The XRD results confirm that the Mg²⁺ metal ions doping into KAP.

3.3 Thermal analysis

3.3.1 Thermogravimetry analysis

In order to identify the thermal stability, purity and crystalline nature of solution grown pure and Mg doped KAP crystals, they were subjected to thermal analysis. The curves of pure and Mg ion doped KAP are shown in fig. 3. Experimentally observed weight loss at various stages of decomposition agrees well with the theoretically calculated values according to the following equations [9]:



The weight loss starts at around 250 °C and about 40% of the total weight loss has occurred during the initial decomposition of both pure and doped KAP according to Eq. (1). The onset temperature of the decomposition was found to be 253, 268, 255 and 282 °C for pure and Mg

(0.1, 0.2 & 0.3 mol %) doped KAP respectively. It can be noted that 0.3 mol % Mg doped sample begins to decompose at a lower temperature of about 50 °C and continuous to lose weight (up to 10%) gradually followed by a sharp weight loss at 290 °C. The low temperature weight loss might be due to the moisture present in the sample. Similar behavior was noticed in case of Ba²⁺ doped KAP crystal [10].

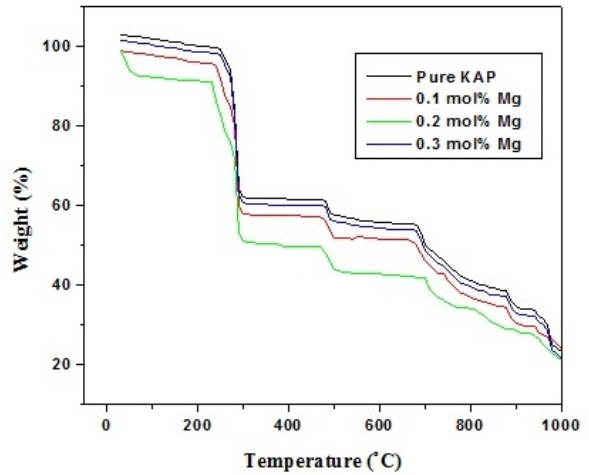


Fig. 3. Thermogravimetric analyses of pure and Mg doped KAP crystals

The total weight loss up to 1000 °C was found to be 80%, 90%, 95% and 82% for pure and Mg (0.1, 0.2 & 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 TGA curves confirm that the Mg²⁺ ions were doped into the crystalline matrix.

3.3.2 Optical transmittance studies

UV-Visible spectral analysis is an efficient tool to determine the optical transparency of the crystals, an important property for a material to be optically active [11]. The as grown crystals of higher quality with thicknesses of 2.4, 2.1, 2.2 and 2 mm for pure and Mg (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 (fig. 4). All the crystals have 35-55% transmittance crystals only at 900-1100 nm. The UV spectrum reveals that the cut off wavelength is ~ 300 nm and a wide transparency in the entire visible region which makes the material suitable for second harmonic generation. All the crystals have sufficient transmission in the visible and near IR region. Pure KAP revealed the highest transmittance of about 55%. On the other hand, the

transmittance was found to be 45%, 35% and 34% for pure and Mg (0.1, 0.2 & 0.3 mol %) doped KAP respectively. The observed decrement in transmittance confirms the doping of divalent ion into KAP.

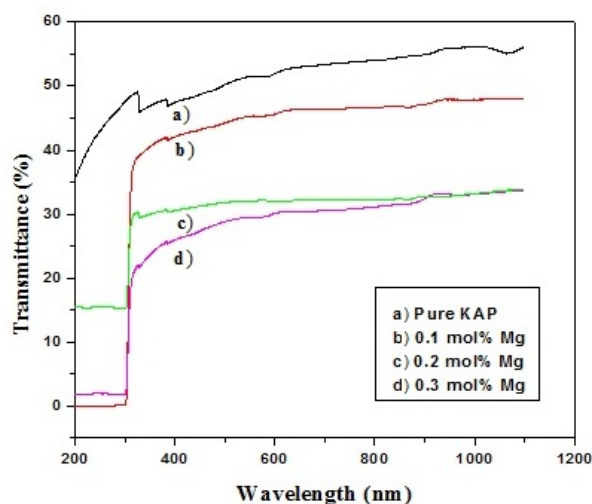


Fig. 4. UV-NIR spectra of KAP crystals; (a) pure, (b) 0.1 mol% Mg, (c) 0.2 mol% Mg, (d) 0.3 mol% Mg

3.3.3 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 Mg doped KAP are shown in fig. 5. 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 1388 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 1561 cm^{-1} remained almost unchanged for both pure and doped KAP [7]. The C=C ring stretching is present around 1476 cm^{-1} for both undoped and doped samples. C-H stretching vibration appears near 2479 cm^{-1} in all the investigated samples. The peak around 3445 cm^{-1} corresponding to O-H stretching hydrogen bond was found to be different significantly in terms of intensity. In exacting, the peak intensity of 3451 cm^{-1} is very strong for Mg (0.3 mol %) doped KAP when compared to the peaks 3440 cm^{-1} and 3425 cm^{-1} for Mg (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.

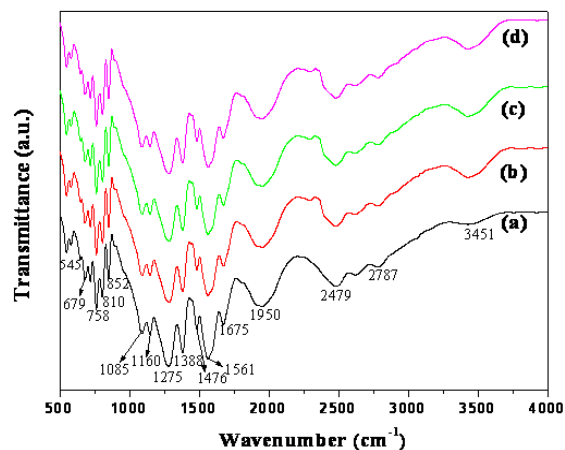


Fig. 5. FTIR spectra of KAP crystals; (a) pure, (b) 0.1 mol% Mg, (c) 0.2 mol% Mg, (d) 0.3 mol% Mg

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

Pure KAP (cm^{-1})	1 mol Mg (cm^{-1})	0.2 mol Mg (cm^{-1})	0.3 mol Mg (cm^{-1})	Assignments
3445	3440	3425	3450	O-H stretching hydrogen bond
2479	2480	2481	2480	-C-H aromatic stretching
1950	1949	1948	1950	C=C asymmetric stretching
1675	1673	1674	1672	C=C stretching
1561	1560	1562	1560	-C=O carboxylic ion=O (A. S)
1476	1477	1475	1477	C=C ring stretching
1388	1387	1389	1388	-C=O carboxylic ion=O (S. S)
1275	1276	1274	1275	C-O stretching
1160	1162	1161	1160	C-C stretching
1085	1084	1086	1088	C-C=O stretching
852	850	851	850	C-H out of plane bending
758	757	759	758	C-C stretching
679	678	680	681	C-O Wagging
545	544	543	545	C-C-C out of plane ring deformation

3.3.4 Microhardness studies

Measurement of hardness is a useful nondestructive testing method to determine the hardness of the material [12]. Vickers microhardness test was carried out on pure and Mg 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 100g. The microhardness values were calculated from the formula $H_v = 1.8544 P/d^2\text{ kg/mm}^2$, where H_v is the Vickers microhardness number, P is the applied load (kg) and d is average diagonal length of the indentation (nm) [13]. The hardness values as a function of load are shown in fig. 6. The result reveals that the microhardness values are higher for 0.3 mol % Mg doped crystal than pure KAP crystal. In contrary H_v value of 0.1 mol % Mg doped crystal decreased when compare to pure KAP crystal. The results suggest that 0.3 mol % Mg doped crystals are preferred for device fabrication than the undoped and 0.1 mol % Mg doped KAP crystals.

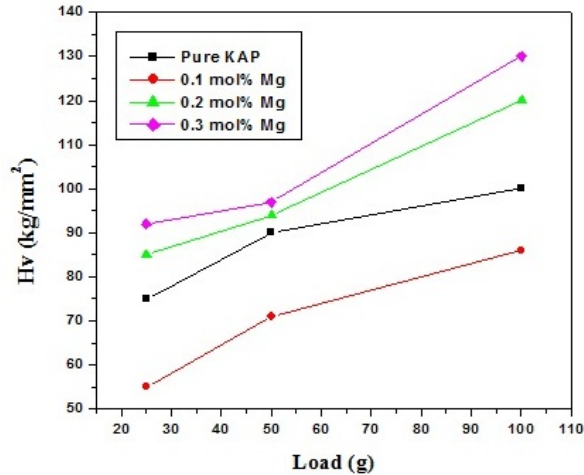


Fig. 6. Dielectric constant vs log frequency measured at 40 °C of pure and mg doped KAP crystals

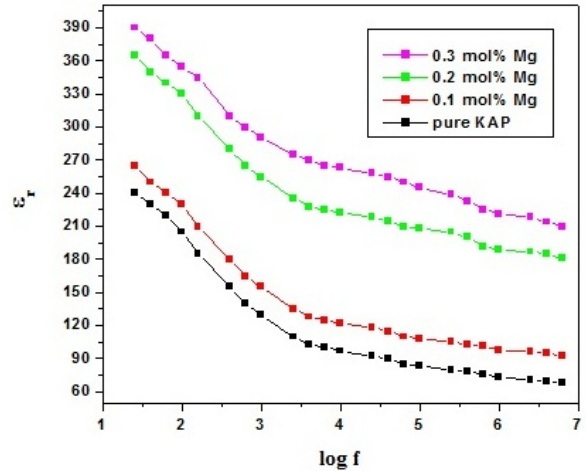


Fig. 7. Dielectric constant vs log frequency measured at 40 °C of pure and mg doped KAP crystals

3.3.5 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 $\epsilon_r = Cd/\epsilon_0A$ and $\tan\delta = D\epsilon$, 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 (8.854×10^{-12} F/m) [14]. The dielectric constant and dielectric loss for pure and Mg ion doped KAP crystals measured at 40 °C are shown in Figs. 7 and 8 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 [15].

The dielectric constant (ϵ_r) values were estimated as 238, 239, 367 and 388 for pure and Mg (0.1, 0.2 & 0.3 mol %) doped KAP respectively. The dielectric constant of 0.3 mol % Mg doped KAP is much higher when compared to that pure and 0.1 & 0.2 mol % Mg doped KAP crystal. The dielectric loss of pure and Mg doped KAP crystals were shown in Fig. 8.

It clearly shows the dielectric loss ($\tan\delta$) value of 0.3 mol % doped KAP crystal has much lower when compare to pure and 0.1 & 0.2 mol % Mg 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 [15].

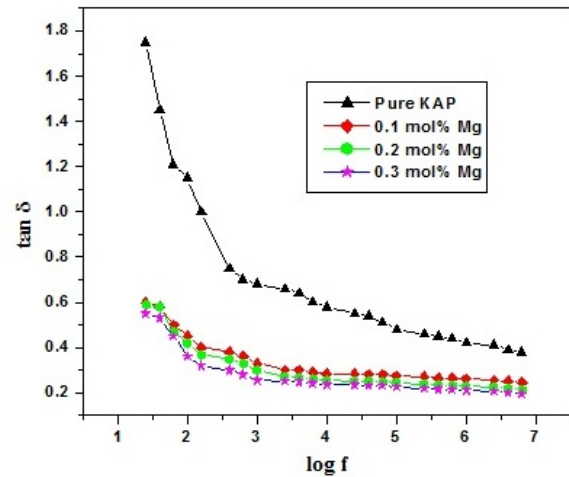


Fig. 8. Dielectric loss vs log frequency measured at 40 °C of pure and mg doped KAP crystals

3.3.6 SHG measurements

In order to confirm the NLO property of the grown crystals, they were characterized SHG measurements. Fig. 9 shows the SHG efficiency of pure and Mg doped KAP crystals. The SHG efficiencies are estimated as 32, 30, 31, 45 mV for pure and Mg (0.1, 0.2 & 0.3 mol %) doped KAP respectively. For KDP it was 31 mV. Thus the SHG efficiency for 0.3 mol % Mg doped crystal was 1.5 times that of the KDP crystal. Hence the 0.3 mol % Mg doped crystals are suitable for device fabrication in NLO technologies than the pure KAP.

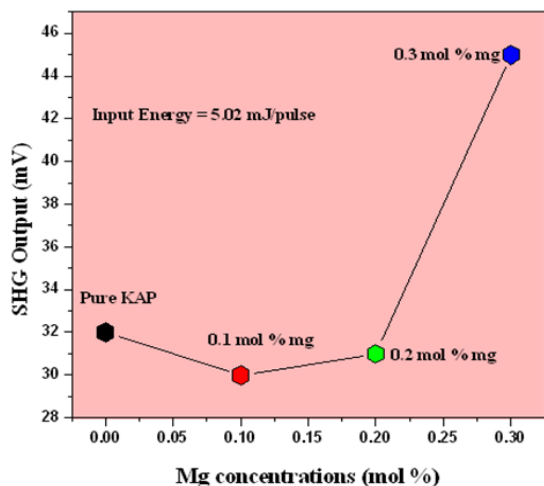


Fig. 9. Shows the SHG efficiency of pure and Mg doped KAP crystals

4. Conclusions

In the present work, we have successfully synthesized good optical quality single crystals of magnesium doped potassium acid phthalate (KAP) by slow evaporation technique at room temperature. Powder X-ray diffraction results confirm that the crystals belong to orthorhombic system. Elemental analysis by ICP-OES confirmed the Mg^{2+} ions doping into the grown KAP crystals. The FTIR spectrum confirmed the presence of functional groups in the pure and doped crystals. 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 Mg^{2+} doped crystals have higher hardness values than that of pristine KAP. Dielectric constant value of Mg^{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 % Mg doped crystals are suitable for device fabrication in nonlinear optical applications.

References

- [1] A. Miniewicz, S. Bartkiewicz, *Adv. Mater. Opt. Electron.* **2**, 157 (1993).
- [2] P. Murugakoothan, R. Mohan Kumar, P. M. Ushasree, R. Jayavel, R. Dhanasekaran, P. Ramasamy, *J. Cryst. Grow.* **207**, 325 (1999).
- [3] B. N. Mavrin, M. V. Koldaeva, R. M. Zakalyukin, T. N. Turskaya, *Opt. Spectrosc.* **100**, 862 (2006).
- [4] R. Ashok Kumar, N. Sivakumar, R. Ezhil Vizhi, D. Rajan Babu, *Physica B: Condensed Matter.* **406**, 985 (2011).
- [5] R. Mohan Kumar, D. Rajan Babu, P. Murugakoothan, R. Jayavel, *J. Cryst. Growt.* **245**, 297 (2002).
- [6] G. Vasudevan, P. AnbuSrinivasan, G. Madhurambal, S. C. Mojumdar, *J. Therm. Anal. Calorim.* **96**, 99 (2009).
- [7] S. Parthiban, S. Murali, G. Madhurambal, S. P. Meenakshisundaram, S. C. Mojumdar, *J. Therm. Anal. Calorim.* **100**, 751 (2010).
- [8] P. Kanchana, A. Elakkina Kumaran, C. Sekar, *Spectrochim. Acta, Part A* **112**, 21 (2013).
- [9] A. Elakkina Kumaran, P. Kanchana, C. Sekar, *Spectrochim. Acta, Part A* **91**, 370 (2012).
- [10] P. Kanchana, A. Elakkina Kumaran, Y. Hayakawa, C. Sekar, *Spectrochim. Acta, Part A* **103**, 187 (2013).
- [11] I. Alessandri, E. Bontempi, L. Sangaletti, S. Pagliara, L. Malavasi, F. Parmigiani et.al. *J. Phys IV France* **118**, 165 (2004).
- [12] R. Uthrakumar, C. Vesta, C. Justin Raj, S. Krishnan, S. Jerome Das, *Curr. Appl. Phys.* **10**, 548 (2010).
- [13] R. Parimaladevi, C. Sekar, V. Krishnakumar, *Spectrochim. Acta, Part A* **75**, 617 (2010).
- [14] R. Parimaladevi, C. Sekar, *Spectrochim. Acta, Part A* **76**, 490 (2010).
- [15] V. Chithambaram, S. Jerome Das, R. Arivudai Nambi, et.al, *Physics B* **405**, 2605 (2010).

*Corresponding author: vijiniraimathi@yahoo.com