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Optical, NLO, dielectric, thermal and hardness properties of mono valent metal ion (Ag^+, Li^+ and Na^+) doped KAP crystals

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ABSTRACT

Crystals of potassium hydrogen phthalate (KAP), a semi-organic compound, have been grown by slow evaporation method at room temperature from aqueous solution in the presence of mono valent metal ionic impurities Ag^+, Li^+ and Na^+. Elemental analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES) proves the incorporation of these impurities into the grown crystals. Powder X-ray diffraction studies confirmed the phase formation and metal ions doping into KAP crystals. Thermo gravimetric *analysis* (TGA) show the onset decomposition temperatures to be 255, 258, 238 and 272°C for pure and Ag^+, Li^+ and Na^+ doped KAP crystals respectively. Microhardness studies revealed that Na-KAP crystals have higher hardness values than all the doped crystal. All the crystal exhibited the second harmonic generation (SHG) conversion efficiency. The grown crystals were also subjected to Fourier transform infrared (FTIR) spectroscopy, UV-Vis spectroscopy studies and dielectric studies. Among the three investigated metal ion impurities, Na^+ ion seem to have positive influence on the growth, mechanical, thermal, dielectric and SHG characteristics of KAP which makes it suitable for limited level of applications.

1.Introduction

Potassium hydrogen phthalate or potassium acid phthalate (KAP) with the chemical formula $K(C_6H_4COOH\text{-}COO)$ is a semi organic salt that belongs to the alkali acid phthalate series. KAP crystallizes in an orthorhombic system with the space group $Pca2_1$ [1]. They are widely used as analyzers in the long wavelength range of the X-ray spectrum and as monochromators in various high- resolution X-ray instruments. KAP exhibits piezoelectric, pyroelectric, ferroelectric, elastic and nonlinear optical properties with long term stability in devices [2-4]. Nowadays KAP crystals are used as substrate for epitaxial growth of oriented polymers [1] and hierarchical growth of organized materials [5]. Several authors have investigated the crystallization of KAP in pure and doped form with various dopants in order to improve the crystal quality, morphology and physical properties [6-8]. The metallic ion dopants (Fe^{3+}, Cr^{3+}, Zn^{3+}, Cu^{3+}, Zn^{2+} and Cu^{2+}) in the KAP crystals are reported to induce significant changes in optical, ferroelectric and non linear optical behaviors [9-10]. Here we have chosen three different mono valent metal ion impurities Ag^+, Li^+ and Na^+ to study their effect on the thermal, dielectric, optical, second harmonic generation efficiency and hardness property of KAP crystal.

2. Experimental

Pure and doped KAP crystals were grown by slow evaporation method at room temperature with double distilled water as solvent. Recrystallised salt of KAP (Merck) was used as source material. Initially saturated KAP solution was prepared at room temperature and filtered using micro filter paper of 0.1µm porosity. The mono valent impurities Ag^+, Li^+ and Na^+ were selected as additives in the form of AgCl, LiCl and NaCl. These impurities were added (0.1M % each) with pure KAP solution and the final solutions were stirred well, filtered and stored in separate beakers covered with perforated sheets. The pH values of all the solutions were found to be 4. The supersaturated solutions in beakers were placed in room temperature. The seed crystals were formed by evaporation of solvent with time interval of 2 to 3 days. The grown seed crystals were harvested and are again placed in the respective mother solutions to reach the even growth of all the faces of the crystals and favorable sizes for characterizations. Finally the crystals were harvested (Fig:1). These crystals were subjected to various characterization studies. The pH values of the final mother solutions after harvesting the crystals were found to be 4.0 as that of initial solution.

Powder X-ray diffraction pattern of all the grown crystals were recorded on Joel JDX 8030 diffractometer (CuKα1 wavelength 1.5406Å). Thermo gravimetric analysis was carried out between 30°C to 1000°C in nitrogen atmosphere using Universal V4.3A TA instrument (SDT Q600 V8.3 Build 101) with the heating rate of 20°C/min. UV-Vis 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 Lambda 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. Micro hardness measurements were carried out using Shimadzu tester. Second harmonic generation (SHG) conversion efficiency of the samples was measured by Kurtz powder method. A Q switched Nd:YAG laser beam of wave length 1064 nm was used within an input energy of 5.02

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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 (Tektronix-TDS 3052).

3. Results and discussion

3.1 Crystal growth

Crystals of KAP were grown by slow evaporation method in the presence of AgCl, LiCl and NaCl dopants (0.1M % each). Colorless transparent crystals grew in the hexagonal form as shown in Fig.1. There has been no significant change in the crystal morphology due to the presence of silver, lithium and sodium ions in the growth environment. Even though there is a slight block patches in the silver doped KAP crystal. The pH values of the mixed solution remained unchanged throughout the growth period similar to the case of pure KAP solution. The presence of mono valent metal ion does not influences changes in crystal growth rate and transparent nature of grown KAP crystals. Hence, the metal ions were expected to replace the potassium ion of the KAP without affecting the carboxylic acid group. This is because, if carboxylate hydrogen is exchanged or substituted, there must be a change in pH value of the corresponding solution.

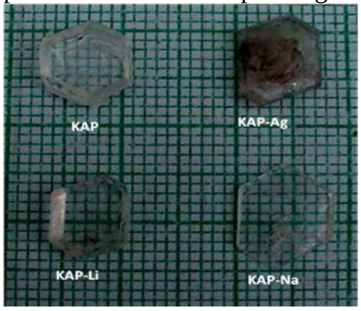

Fig 1. As grown KAP crystals :KAP(pure KAP),KAP-Ag(silver doped) ,KAP-Li(Lithium doped),KAP-Na(sodium doped) KAP crystals.

Inductively coupled plasma-optical emission spectrometric (ICP-OES) analysis confirmed the presence of dopants in the order of 0.031, 0.030, and 1.283mg/L for Ag, Li and Na respectively. It can be noticed that the Na has highest doping level when compared to the other dopants. 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 lattice parameter of the samples was calculated from the equation for the orthorhombic system using the method of least squares.

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

$1/d^2 = h^2/a^2+k^2/b^2+l^2/c^2$ and volume V= abc.

Were d is the lattice spacing, h. k. l is the Miller indices, a, b and c is the lattice parameters λ is the wavelength (CuKα=1.5406 A°) and 2θ is the diffraction angle. The calculated lattice parameters are presented in Table: 1, it suggest that a certain amount of mono valent dopants have been doped into the KAP system.

3.2 Powder X-ray diffraction analyses

Powder XRD patterns of the grown crystals are shown in Fig. 2. The results confirmed that both the undoped and doped KAP crystallized in orthorhombic system with space group $Pca2_1$ according to JCPDS data (31 - 1855 and 24 - 1870). It concludes that the dopant does not change or induce any change in crystal structure.

Table 7.1.Lattice parameters of pure and doped crystals.

Lattice parameters	Pure KAP	Ag-KAP	Li-KAP	Na-KAP
a(Å)	9.31	9.51	9.56	9.47
b(Å)	12.56	12.65	12.78	12.60
c(Å)	6.57	6.55	6.58	6.64
Volume (Å)	767.6	787.8	804.0	792.7

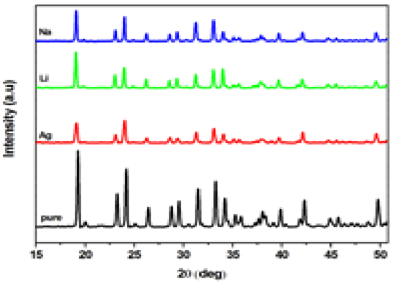

Fig.2 Powder X-ray patterns of KAP crystals; (a) pure KAP, (b) Ag doped, (c) Li doped and (d) Na doped.

3.3 Thermal analyses

The DTA curves of pure and Ag^+, Li^+ and Na^+ doped KAP are shown in Fig. 3. In case of pure sample, experimentally observed mass losses at various stages of decomposition agree well with the theoretically calculated values according to the following equations

$2KC_8H_5O_4 \rightarrow K_2C_8H_5O_4 + C_7H_5O_2 + CO_2$ ----------- (1)

$K_2C_8H_5O_4 \rightarrow K_2CO_3 + C_7H_5O$ ----------- (2)

The weight loss begins at around 250˚C and about 40% of the total mass loss has occurred during the initial decomposition of both pure and doped KAP according to eqn.1. The accurate onset decomposition temperature of the investigated samples was found to be 255, 216, 164, and 173ºC for pure and doped Ag^+, Li^+ and Na^+ KAP respectively. However, the Li-KAP began to decompose at lower temperature of 164˚C and its total weight loss is significantly higher when compared to the other samples. This result suggests that the Li-KAP has reduced thermal stability. Newkirk et al [11] and Belcher et al [12] have carried out an extensive studies on thermal behavior of KAP in N_2 and air atmospheres. The results obtained for pure KAP in the present work agrees well with these reported results.

The total mass loss up to 1000˚C was found to be 81%, 93%, 94% and 91% for pure and Ag^+, Li^+ and Na^+ doped KAP crystals respectively. The results again show the highest mass loss for the Li doped KAP crystals which could be attributed to poor crystallanity of Li-KAP. The occurrence of sharp endothermic peak at around 300˚C in all the investigated samples corresponds to the phase transition according to eqn.1. A significant difference in the high temperature region of the TGA curves of the doped samples confirms that the metal ions are doped into KAP.

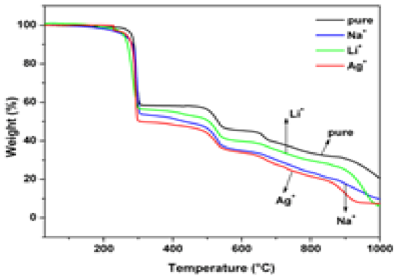

Fig 3. TGA curves of pure and Ag^+, Li^+ and Na^+ doped KAP crystals.

3.4 Optical transmission analyses

Good optical transmittance and lower cut-off wavelengths are very important properties for NLO crystals. The grown crystals of higher quality with thicknesses of 2.5, 2.4, 2.6 and 2.2 mm for pure, Ag^+, Li^+ and Na^+ doped KAP respectively were placed in the crystal holder and the UV-NIR ray of wave length between 190 to 1000 nm was allowed to pass through the (010) face of the grown crystals. There was a large absorption in the region around 300 nm for all the investigated samples (Fig.4) which is due to the n-π transition of the carbonyl group of the carboxyl functions [13]. All the crystals have sufficient transmission in the visible and near IR region. Na doped KAP have the highest transmission of 53% from 400nm to 1100nm. The transmission was found to be lower for all other crystals. The observed decrement and increment in transmission confirms the doping of mono valent ion into KAP crystal sites.

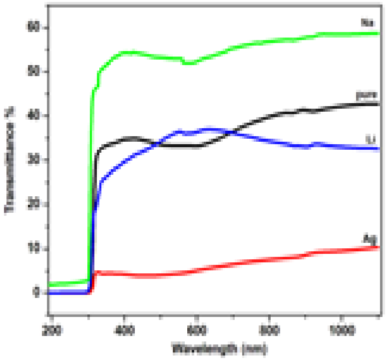

Fig 4. UV-Vis spectrum of as grown pure and doped KAP crystals.

3.5 FTIR analyses

FTIR spectra of the as grown KAP crystals are shown in Fig. 5. The vbrational assignments of the as grown crystals were cited in Table. 2. The broad peak around 3430 cm^{-1} is due to O-H stretching hydrogen bond. The absorption peak in the region less than 900 cm^{-1} appears due to C-H bending vibrations. The asymmetric stretching modes of vibrations of –C-O are observed at 1566, 1574, 1571, and 1566 cm^{-1} for pristine and Ag^+, Li^+ and Na^+ doped KAP respectively. The strong hydrogen bonding interaction of C-OH group and corresponding C-OH in plane and out of plane bands are observed as weak band at around 1482 cm^{-1} and 850 cm^{-1} respectively [14]. The slight change in the peak region of 3250 to 3450 cm^{-1} also could be the evidence for the doping of metal ion.

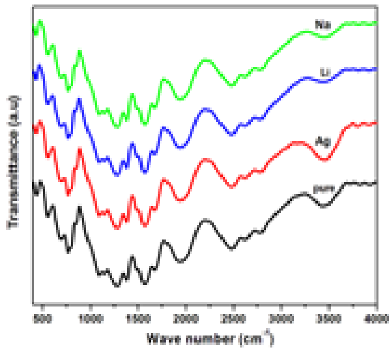

Fig.5 FTIR spectrum of pure and doped KAP crystals.

Table 7.2. Vibrational assignments of pure and doped KAP crystals.

Pure KAP cm^{-1}	Ag-KAP cm^{-1}	Li-KAP cm^{-1}	Na-KAP cm^{-1}	Tentative assignments
406	411	409	412	C=C out of plane bending
440	441	441	441	C=C out of plane ring bending
548	549	549	550	C=C-C out of plane ring deformation
581	582	581	580	C=C-C out of plane ring deformation
642	642	648	650	C=C out of plane bending
683	682	682	683	C-O wagging
718	718	718	719	=C-H out of plane deformation
762	763	762	764	C-C stretching
802	804	807	805	C=H out of plane bending
848	849	850	850	C-H out of plane bending
891	890	888	892	=C-H out of plane bending
1090	1090	1090	1091	C-C-O stretching
1146	1146	1147	1147	C-C stretching
1280	1281	1284	1284	C-O stretching
1380	1380	1382	1379	-C=O Carboxylate ion =O symmetric stretching
1482	1483	1484	1483	C=C ring stretching
1566	1581	1560	1580	-C=O Carboxylate ion asymmetric stretching
1670	1669	1669	1668	C=C stretching
2480	2482	2481	2483	O-H Hydrogen bonded
2620	2620	2620	2620	O-H stretching
2790	2804	2802	2789	O-H stretching
3431	3430	3425	3433	O-H stretching Hydrogen bond

3.6 Dielectric studies

Dielectric constant as a function of frequency was measured using samples with dimensions of 1.72, 1.40, 1.80, and 1.59 mm for pure, Ag^+, Li^+ and Na^+ doped KAP respectively. Graphite was applied on opposite sides of the crystals and the samples were placed between two copper electrodes and thus parallel plate capacitors were formed. Capacitances of the samples were measured for various frequencies in the log frequency range of 1.5 Hz to 6 Hz, at fixed temperature of 100°C. Dielectric constant is calculated using the relation $\varepsilon_r = Cd/\varepsilon_0 A$ where C is the capacitance, d is the thickness of the crystal, A is the area of cross-section and ε_0 is the absolute permittivity of the free space [10].

The variation of dielectric constant with frequency at 100°C is shown in Fig. 6. It has slight high values at low frequency region and these values decreases with increase in applied frequency for all the crystals. In the low frequency region, dielectric constant of all doped and pure crystals was found to be high values. These higher values of dielectric constant in the low frequency region are due to the fact that all the four polarizations such as space charge, orientational, electronic and ionic polarization are present initially. Its low values at high frequencies could be due to the loss of importance of these polarizations. The corresponding dielectric losses for all the investigated crystals at 100°C are shown in Fig.7. The low values of dielectric constant and loss to Na-KAP in the low frequency region suggest that the grown crystal possess good optical quality. This parameter is of vital importance for nonlinear optical applications [15]. The slight increase in the value of dielectric constant for all other metal ion doped KAP crystal (except Na-KAP) at low frequency region may be due to the stray in capacitance [16].

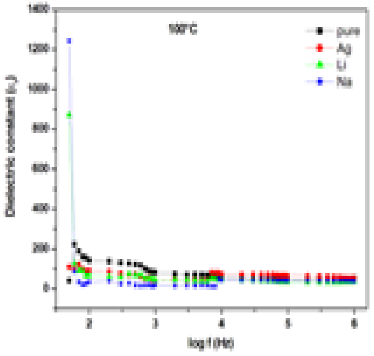

Fig 6. Dielectric constant verses log frequency measured at 100°C.

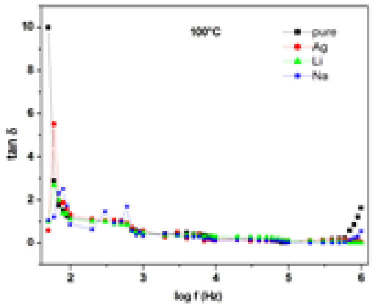

Fig 7. dielectric loss verses log frequency measured at 100°C.

3.7 Vickers microhardness studies

Hardness testing is often the only mechanical property test that can be applied to hard solids. It plays key role in device fabrication. Microhardness measurements were carried out using Shimadzu tester with the applied loads of 25, 50 and 100g. Indentations were made on (010) face of the pure and doped KAP crystals. Vickers micro hardness values were calculated from the formula Hv=1.8544 P/d^2 kg/mm^2, where P is the applied load in gram and d is average diagonal length of indentation mark in micro meter. Fig. 8 shows the hardness values of all the grown crystals as a function of load. The hardness values of Na doped crystal higher than that of all other doped crystal. The hardness values increased with increase in load for all pure and doped KAP crystal up to 100 gram load. But if the load increased more than 100 gram crack has developed in the crystal. The observed increase in hardness values with increasing load for all the investigated samples can be understood based on the reverse indentation size effect.

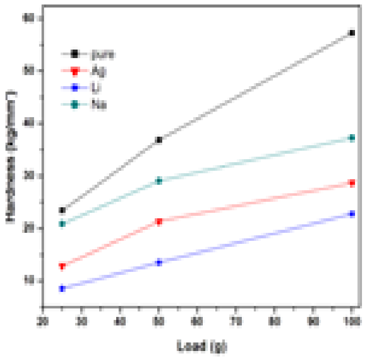

Fig:8 microhardness number verses load for pure and doped KAP crystals.

3.8 SHG measurements

In order to confirm the NLO behavior of metal ion doped KAP, powdered samples were subjected to Kurtz and Perry powder technique which remains powerful tool for initial screening of materials for SHG [17]. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation (λ=534 nm) from the crystal. The SHG efficiencies were found to be 8.6, 7.7, 7.2 and 8.4 mV for pure and Ag, Li and Na doped KAP crystals.28mV for the standard potassium dihydrogen phosphate (KDP) crystal. The conversion efficiency of Na-KAP is nearly 30% of KDP.

4. Conclusions

Optically transparent KAP crystals were grown by slow evaporation method from the individual mixtures of AgCl, LiCl and NaCl with KAP. The powder XRD studies and elemental analysis by ICP-OES confirmed the metal ions doping into the sites of grown KAP crystals. TGA results revealed that the onset decomposition temperature of Li-KAP is lower and its total weight loss (98 wt. %) is higher when compared to that of all the other investigated crystals. It shows that the Li-KAP have reduced thermal stability. The result suggests that Li-doping into KAP reduces its thermal stability. It also reflected in hardness study. The optical transmission studies confirmed that the metal ion Ag and Li doping reduces the optical quality of the KAP crystal, contrary to this the Na doping increases the optical quality of the KAP crystal. The hardness values of Na doped crystal have higher than that of other doped KAP crystal. There has been a considerable positive influence on Na-KAP in optical, dielectric, thermal stability and SHG efficiency.

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