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A study on the growth, optical, thermal, mechanical, dielectric and piezoelectric properties of dye doped KAP single crystals

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ABSTRACT

Potassium hydrogen phthalate single crystals have been grown by conventional and Sankaranarayanan–Ramasamy method. Dye inclusion crystals have attracted researchers in the context of crystal growth for applications in solid state lasers. The effect of crystal violet as dopant on the characteristic properties of KAP crystal was studied. Thermal stability of the crystals is tested using TG-DTA. There is only one endothermic peak which indicates the decomposition point. The optical transparency of the crystals was identified from the UV–vis spectrum. The mechanical strength of the crystals has been measured by Vickers micro hardness. The dielectric, piezoelectric and luminescence study is carried out for both pure and dye doped KAP crystals. The photoluminescence spectrum of the KAP induced by the dye-doping reveals an emission band peaking at 595 nm.

1. Introduction

The potassium hydrogen phthalate(KHP) with chemical formula $K(C_6H_4COOH–COO)$ also known as potassium acid phthalate (KAP) is a semiorganic compound and crystallizes in orthorhombic system with the space group of $Pca2_1$ and its lattice parameters are $a = 9.605$ Å, $b = 13.331$ Å, $c = 6.473$ Å and $\alpha = \beta = \gamma = 90^\circ$ [1,2]. Potassium hydrogen phthalate crystals are easily grown from slow evaporation solution growth with water as a solvent and it has 14 natural growth faces with dominating (0 1 0) face. The (0 1 0) face is more suitable for any surface morphological studies [3]. Potassium hydrogen phthalate crystals were studied intensively, since they started to be used as X-ray monochromators and X-ray analyzers. They exhibit piezoelectric, pyroelectric, ferroelectric, elastic and nonlinear optical properties with long term stability in devices [4,5]. Recent papers showed interesting optical properties of dye doped single crystals such as KAP [1,6]. The up-conversion luminescence due to second harmonic generator properties of the KAP crystals doped with different dyes has been investigated [7–9].

Dye inclusion crystals are used for application of solid state lasers. The dye molecule is incorporated with the water soluble crystals and avoids many drawbacks like other solid materials such as working media for lasers. Dyes do not interact with oxygen and water [10]. The dyes absorb in the visible range of 500–550 nm. Thus second harmonic generation of Nd-YAG laser light is suitable for pumping the dyes in order to achieve lasing effect [11]. Due to broad absorption in the visible region in the dye doped crystal it can be used as a filter. Several other crystals such as potassium nickel sulfate hexahydrate and cesium nickel sulfate hexahydrate are reported being used as filters [12,13]. The effect of dye rhodamine 6G and coumarin 6 on potassium hydrogen phthalate was studied by Enculescu et al. [6,14]. An easily growing non-linear optical (NLO) single-crystalline material that combines the qualities of liquid dye-lasers such as high efficiency and broadband tunability with the flexibility and the convenience in operation offered by a single crystal is a very interesting alternative. Such an alternative may be represented by the dye doped single crystals of KAP [14].

The lowest concentration of some organic impurities, such as Chicago sky blue, amaranth and sunset yellow could slightly distort the KDP lattice and thereby introduce local deformations, which are assumed to be the original reason that causes the changes of optical properties [15–18]. Crystal violet (CV) is one of the cationic

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organic dyes whose tinctorial values are very high, less than 0.1 mol% of the dye produces an obvious coloration [19]. However, there is no data in the addition of CV with KAP single crystals.

The effect of crystal violet as dopant on the characteristic properties of KAP crystal was studied by both conventional and Sankaranarayanan–Ramasamy(SR) method. It is possible to grow large size good quality crystals by selecting specific orientation using SR method. For device fabrication we need a large size, mechanically and optically good quality single crystal. This paper presents the influence of crystal violet dye on the optical transmission, mechanical hardness, thermal stability, piezoelectric, dielectric and photoluminescence properties of potassium acid phthalate single crystals.

2. Experimental and crystal growth

2.1. Crystal growth by conventional method

Saturated solution of pure KAP is obtained by dissolving potassium hydrogen phthalate in double distilled water (18.2 MΩ cm resistivity) and 0.1 mol% of crystal violet is added to this solution. It has been stirred continuously for 4 h using magnetic stirrer for homogenization. Final solution is filtered and it is kept for slow evaporation at room temperature and thereafter bluish transparent crystals have been harvested with dimensions up to $10 \times 6 \times 3$ mm^3. The conventional method grown pure KAP is shown in Fig. 1(a) and dye doped KAP is shown in the Fig. 1(b).

2.2. Crystal growth by SR method

The experimental setup for unidirectional growth was described in the earlier reports [20,21]. A good quality crystal obtained from conventional slow evaporation method is selected as a seed by choosing (0 1 0) face. It is mounted in the bottom of a cylindrical glass ampoule of 10 mm diameter and 150 mm length. Saturated solution was prepared at room temperature (32 °C) and it was filled into the seed loaded ampoule. The temperature at bottom portion was maintained at 32 °C and top portion of the ampoule was maintained at 37 °C for evaporation. The top portion of the ampoule is closed with a plastic sheet to control the evaporation rate and to restrict the dust particles entering into the saturated solution, which may lead to surface nucleation. After the seed was mounted in the ampoule the growth could be seen visually on the 11th day, thereafter a good quality crystal of size 33 mm in length and 22 mm maximum diameter was grown with the average growth rate of 1.5 mm/day. As grown crystal, grown by SR method is shown in Fig. 1(c) and cut and polished crystal discs are shown in Fig. 1(d).

2.3. Characterization

The lattice parameter of the grown crystal is conformed using the Enraf-nonious CAD4 diffractometer with M_ok_α single crystal XRD instrument. UV–vis transmittance spectra were recorded for conventional and SR method grown dye doped KAP crystals with 2 mm thick disc cut along (0 1 0) using PerkinElmer UV–vis–NIR spectrophotometer in the range between 200 and 1100 nm and the slit width is 2 nm [22]. The photoluminescence spectrum of dye doped KAP crystal with 2 mm thickness was recorded at room temperature using a Jobin Yvon-Spex Spectrofluorometer. Microhardness studies are carried out in the (0 1 0) face for both conventional and SR method grown CV doped KAP crystals using the Mututoyo Model MH112 hardness tester. Loads of different magnitudes were applied with indentation time fixed as 5 s for all the crystals. Thermo gravimetric and differential thermal analysis was carried out using PerkinElmer diamond TG/DTA analyzer in the temperature range from 35 °C to 400 °C in the presence of nitrogen atmosphere. The piezoelectric studies were carried out using piezometer system. A precision force generator applied a calibrated force (0.25 N) which generated a charge on the

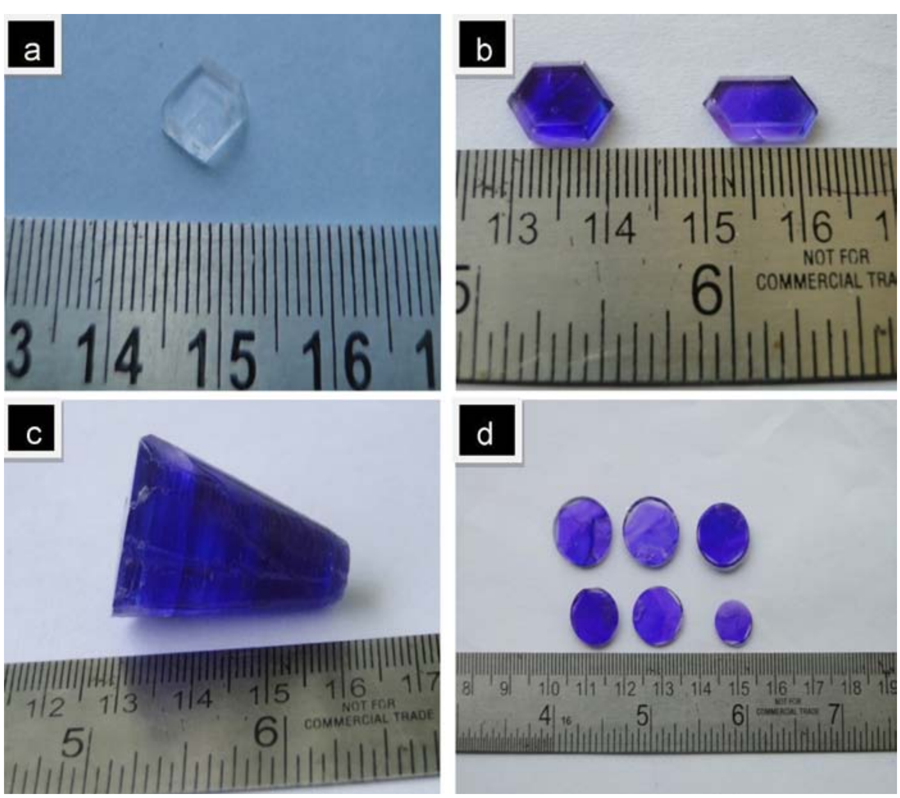

Fig. 1. Crystals grown by (a) conventional method grown pure KAP (b) dye doped KAP (c) SR method grown dye doped KAP (d) cut and polised crystal ingot.

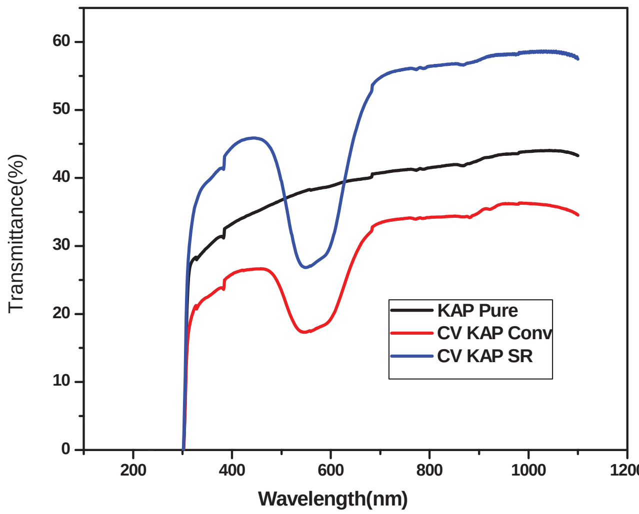

Fig. 2. UV–vis analysis of pure and dye doped KAP single crystals.

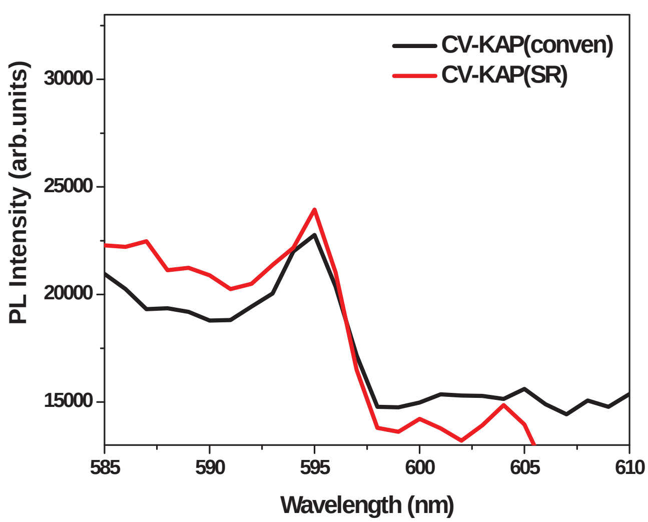

Fig. 3. Photoluminescence spectra of the conventional and SR grown KAP crystal.

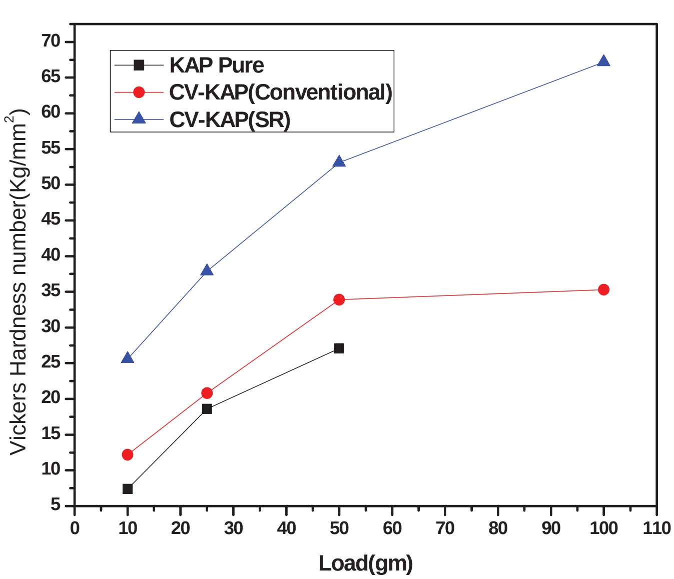

Fig. 4. Vicker's hardness measurement for dye KAP crystals.

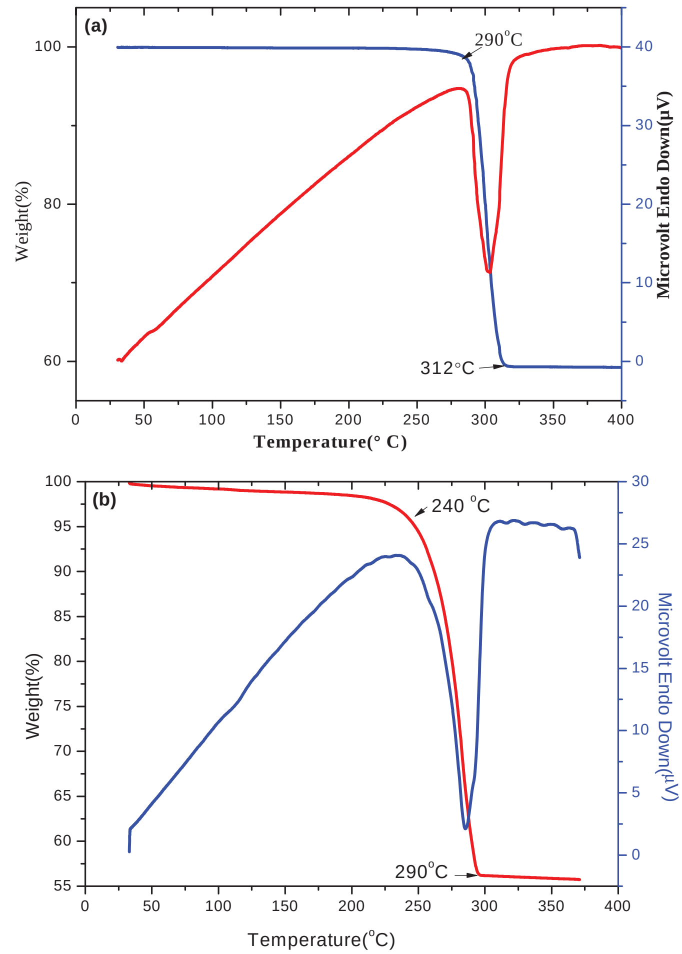

Fig. 5. TG-DTA curve of (a) KAP pure (b) dye doped KAP crystal.

piezoelectric material under test. The output was measured directly from oscilloscope which gives the d_{33} coefficient in units of pC/N. The crystal sample was 1 mm thick and piezoelectric measurement was carried out without poling the sample. Using Agilent 4284-A LCR meter, the capacitances of the crystals were measured for the frequencies 1 kHz, and 1 MHz at various temperatures. The dielectric constants of the crystal were calculated using the relation $\varepsilon_r = C_{crys}/C_{air}$, where C_{crys} is the capacitance of the crystal and C_{air} is the capacitance of same dimension of air. A sample of dimension $8 \times 8 \times 2\,mm^3$ having silver coating on the opposite faces was placed between the two copper electrodes and thus a parallel plate capacitor was formed.

3. Results and discussion

3.1. Single crystal X-ray diffraction

Potassium acid phthalate belongs to orthorhombic system with the space group of $Pca2_1$ and its lattice parameters are $a = 6.463$ Å, $b = 9.623$ Å, $c = 13.271$ Å and volume $v = 825.5$ Å^3 and the angles $\alpha = \beta = \gamma = 90^\circ$. The observed results are in good agreement with previously reported results [2]. This indicates that there is no variation in the structure due to the addition of dye.

3.2. UV–vis NIR analysis

UV–vis–NIR studies give important structural information because the absorption of UV and visible light involves promotion of the electrons in π and σ orbital from the ground state to higher

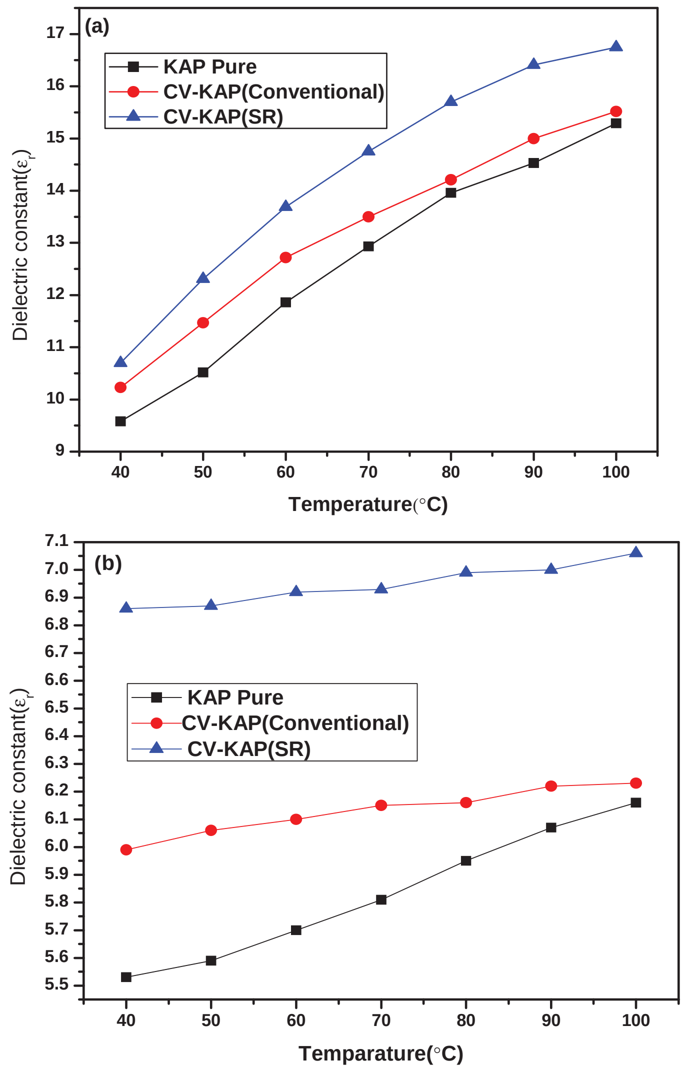

Fig. 6. Temparatre verses dielectric constant at (a) 1 kHz (b) 1 MHz.

energy states. SR method grown crystal shows higher transmittance compared to the conventional method grown crystal (Fig. 2). No changes have been observed in the cut off wavelength and it is nearly 300 nm. The desired lower cut off in the transmittance is between 200 and 400 nm for effective optical applications [23]. There is no significant absorption in the range 300–1100 nm for pure KAP crystals. A prominent characteristic absorption edge is observed at 300 nm in all the cases. In the case of dye-doped KAP, a broad absorption peak between 450 nm and 650 nm has been observed which is more prominent in the case of dye doping. Several researchers reported the appearance of such band due to the incorporation of dye [24–27]. The strong absorption in the visible region (450 nm–650 nm) and the higher transmission in the region (300 nm–450 nm) for dye doped crystal can be of use as filters. The good transparency with lower cut off wavelength at 300 nm makes this material useful for optoelectronics applications [27].

3.3. Photoluminescence studies

Fig. 3 shows a sharp emission band at 594 nm for excitation wavelength 565 nm for dye doped crystals. The intensity of the luminescence is high and the photostability is noticeable. Monica Enculescu [1] studied the photoluminescence properties of different dyes doped KAP single crystal. The results are in good agreement with the present results. Addition of CV in the KAP causes a sharp emission band.

3.4. Vickers micro hardness studies

Hardness is the resistance offered by a solid to the movement of dislocation. Due to the application of mechanical stress by the indenter, dislocations are generated locally at the region of the indentation. H_v was calculated using the formula $H_v = [(1.8544P)/d^2]$kg/mm^2 where P is the applied load in kg and d is diagonal length of indentation in mm. The plot load versus hardness number for the grown crystal is shown in Fig 4. The conventional method grown KAP pure crystals 50 g, thereafter the crackes are developed around the indentation region. Dye doped crystals withstand up to 100 g. The hardness value of SR method grown crystal is higher compared with hardness value of conventional method grown crystals. The higher hardness value of SR method grown crystals indicates a grater stress required to create dislocations thus confirming greater crystalline perfection [28].

3.5. Thermal analysis

TG and DTA curve for pure and CV doped KAP crystal is shown in Fig 5. There is no weight loss up to 280 °C and the decomposition starts at about 290 °C for pure KAP. The 40% of the compound decomposed between 290 °C and 312 °C. In case of dye doped KAP there is gradual weight loss from the beginning and around 240 °C the decomposition ends. When compared to pure KAP, in the decomposition temperature, a difference of 50 °C has been observed in the dye doped KAP. This may be due to the presence of CV in the crystal lattice of KAP. The change in decomposition temperature is due to the incorporation of crystal violet molecule in to the KAP crystal lattice. The crystal violet has low decomposition point compared with KAP and low decomposition temperature of the crystal violet reduces the decomposition temperature of the KAP. The similar results are observed in several articles like DL-malic acid doped ADP [29], oxalic acid doped ADP [30].

3.6. Piezoelectric studies

The piezoelectric substance is one that produces an electric charge when a mechanical stress is applied. The obtained piezoelectric coefficient (d_{33}) value for conventional method grown pure KAP is 0.36 pC/N, dye doped conventional KAP is 0.71 pC/N and SR grown crystal is 2 pC/N. Higher d_{33} value was observed for dye doped conventional and SR method grown crystal when compared to the pure KAP. The results indicate that the presence of dyes has influenced the piezoelectric nature of the crystal.

3.7. Dielectric study

Figs. 6 and 7 show the dielectric constant and dielectric loss as a function of temperature respectively. It can be seen that the dielectric constant increases with increasing temperature after 1 kHz and it is almost saturated when the frequency is increased to 1 MHz. This may be due to the fact that at lower frequencies all the polarizations are active whereas in the case of high frequency, i.e., above 1 MHz only electronic and ionic polarizations are active. Those polarizations are independent of temperature [31,32]. It is observed from the Figs. 6 and 7 that the dielectric constant for SR method grown crystal is high and the dielectric loss is low. The presence of dyes increased the dielectric constant for the SR method grown crystals due to the uniform distribution of the dye molecules in the crystal lattice. These results are strongly correlated with piezoelectric results.

4. Conclusion

Crystal violet dye was successfully doped in KAP and the dopant can affect the various properties of pure KAP. Crystal violet doped potassium hydrogen phthalate is grown by conventional method and (0 1 0) directed crystal of size 20 mm in diameter and 33 mm in length with higher growth rate has been grown using SR method. The SR method grown crystals show good transmittance compared to the conventional method grown crystal and it has lower cut off at 300 nm. The strong absorption in the visible region and high transmittance in the near UV region can be used as filters. Hardness of SR method grown crystal is higher than that of the conventional method grown crystals. Larger hardness value of SR method grown CV-KAP crystal indicates greater stress required to form dislocation thus confirming greater crystalline perfection. From the dielectric study it is observed that dye doped crystal has higher dielectric constant and lower dielectric loss at various temperatures. The piezoelectric nature of the dye doped KAP crystal is increased compared to the pure KAP crystal due to incorporation of dye molecule in the crystalline lattice. Dye doped KAP crystals exhibit a sharp emission band at 594 nm when excited with 565 nm. The absorption at visible region and sharp emission band indicate the presence of CV in the KAP crystal.

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