

## **GROWTH, STRUCTURAL, THERMAL AND OPTICAL PROPERTIES OF Mg<sup>2+</sup>-Co<sup>2+</sup> DOPED POTASSIUM ACID PHTHALATE CRYSTALS**

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### **ABSTRACT**

Single crystals of pure potassium acid phthalate (KAP) and magnesium-cobalt (Mg<sup>2+</sup>-Co<sup>2+</sup>) co-doped potassium acid phthalate crystals were grown by an isothermal evaporation method. Optically transparent and coloured KAP single crystals were grown by doping divalent bimetallic impurities. Enhancement of the metastable zonewidth was achieved by the addition of co-doped bimetallic impurities in KAP solution. It is anticipated that these larger cations play a vital role in the growth mechanism and it favours to reduce the formation of secondary nucleation by positioning the doped metal ions into the interstitial sites. The XRD results confirm that the incorporation of bimetallic ions into the KAP crystal lattice. The optical transmission is found to decrease in Mg-Co doped crystals compared to that of pure KAP.

Key words: Growth, Structural, Optical properties, Doped potassium acid, Phthalate crystals

### **INTRODUCTION**

Potassium acid phthalate (KAP), K.C<sub>6</sub>H<sub>4</sub>COOH.CO<sub>2</sub>, is a promising semi-organic crystal and it crystallizes into the orthorhombic form with four molecules per unit cell and space group Pac<sub>2</sub><sub>1</sub> (Geetha *et al.* 2006) KAP single crystals exhibit excellent physical properties and also piezoelectric, pyroelectric and nonlinear properties (Kejalakshmy and Srinivasan 2004). It is widely used as X-ray monochromator and X-ray analyzer.

Many studies on the growth kinetics of KAP doped with different impurities were reported (Hottenhuis and Lucasius 1986, Mohan Kumar *et al.* 2002, Murugakoothan *et al.* 1999, Uthayarani *et al.* 2008). Presence of small amount of impurities in the form of an ionic bimetallic dopant Mg<sup>2+</sup>-Co<sup>2+</sup> plays a vital role on the growth rate, habit of the crystal and its properties. In order to grow bulk crystals with faster growth rates along all the crystallographic directions, the solubility, metastable zonewidth, induction period and nucleation parameters such as radius of critical nucleus, critical free energy, etc. are necessary information to optimize the growth conditions. The addition of some transition metal ions as impurities is expected to influence the growth kinetics, habit modification as well as size of

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single crystals. In the present work, bimetallic dopants were added to see the role of impurities on growth, thermal, optical and structural changes and the quality of the KAP crystal.

## MATERIALS AND METHODS

The solubility of KAP in pure state and KAP doped with bimetallic impurities were determined in the present study. Cobalt sulphate ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ) and magnesium sulphate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) were used as sources of  $\text{Co}^{2+}$  and  $\text{Mg}^{2+}$  cations. Analar grade KAP ( $\text{C}_8\text{H}_5\text{O}_4\text{K}$ ), E-Merck, and double distilled water were used in the present study. The mother solution was prepared using the solubility relation (Begum 2009),

$$C(T) = 9.283 - 0.059 T + 0.0058 T^2 \text{ of KAP in water}$$

where  $C(T)$  is the solubility of KAP in water (g/100 ml) and  $T$  is the temperature ( $^\circ\text{C}$ ). The solution was stirred using an immersible teflon coated magnet continuously for six hours to achieve stabilization. Using this technique, the authors evaluated the magnitude of solubility of KAP for various temperatures ( $30 - 50^\circ\text{C}$ ). The solubility curve of pure KAP is shown in Fig. 1.

*Metastable zonewidth:* The saturated solution of KAP and CMKAP were prepared in accordance with the solubility data for the nucleation experiments. Hence the metastable zonewidth of above saturated solution was measured by the conventional polythermal method (Rajesh *et al.* 2002). These studies were carried out in a constant temperature bath (accuracy  $\pm 0.1^\circ\text{C}$ ). A constant volume of 100 ml solution was used in all the experiments. The saturated solution was preheated to  $5^\circ\text{C}$  above the saturation temperature for homogenization and the solution was maintained at the super heated temperature for 1 hour before cooling. The solution was continuously stirred using an immersible teflon coated magnet to ensure homogeneous concentration. In the polythermal method, the equilibrium saturated solution was cooled from the over heated temperature till the temperature at which the first visible critical nucleus was observed. The direct visual method was adopted for studying the nucleation temperature. The difference between the saturated temperature and the nucleation temperature is taken to be the metastable zonewidth of the system. The experiment was repeated for saturation temperatures, 35, 40, 45 and  $50^\circ\text{C}$ . The metastable zonewidth for different saturation temperatures for pure and bimetallic doped solutions are shown in Fig. 1.

*KAP and bimetallic doped KAP crystal :* For bimetallic crystallization of KAP, magnesium sulphate, cobalt sulphate and KAP, were taken in the molar ratios (1 : 0.01 : 0.5). In the present study, solution growth by slow evaporation technique at room temperature was adopted to grow KAP and CMKAP crystals.

At room temperature, saturated solution was prepared in individual cases. The solution was filtered and kept in a Petri dish and allowed to evaporate in a dust free

atmosphere. Good quality transparent defect free seed crystals were prepared by natural evaporation technique. Optically good and bulk crystals (pure and doped KAP) having dimensions  $7 \times 6 \times 1.5 \text{ mm}^3$  to  $18 \times 16 \times 3 \text{ mm}^3$  with perfect external morphology were harvested within a period of 15 days and are shown in Fig. 2. Certain bimetallic ions like ( $\text{Mg}^{2+}$ - $\text{Co}^{2+}$ ) doped with KAP taken in the molar ratios (1 : 0.01 : 0.5) produced redish brown (Begum 2009). The grown crystals doped with bimetallic impurities have similar morphology as that of the pure one.

## RESULTS AND DISCUSSION

The metastable zonewidth of KAP and CMKAP solutions is shown in Fig. 1. It is obvious from Fig. 1 that the zonewidths for all the solutions decrease as the temperature increases. At the same time, addition of bimetallic dopants enhances the metastable zonewidth of KAP solutions for all the temperatures. Also, it is observed that during the

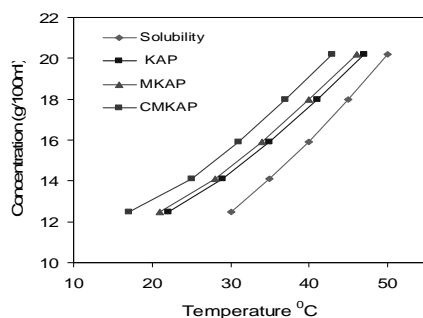


Fig.1. Solubility and metastability limit curves for pure and bimetallic doped KAP.

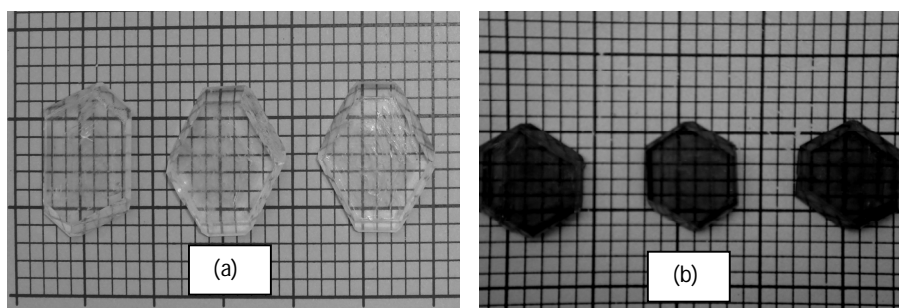


Fig. 2. Photographs of as grown (a) pure KAP, (b)  $\text{Co}^{2+}$ - $\text{Mg}^{2+}$  doped KAP crystals.

experiment, the number of tiny crystals formed by spontaneous nucleation is appreciably reduced in presence of bimetallic dopants compared to that of pure one. This might be due to the incorporation of bimetallic impurities, which might reduce the heterogeneous nucleation, thereby causing to form minute crystals.

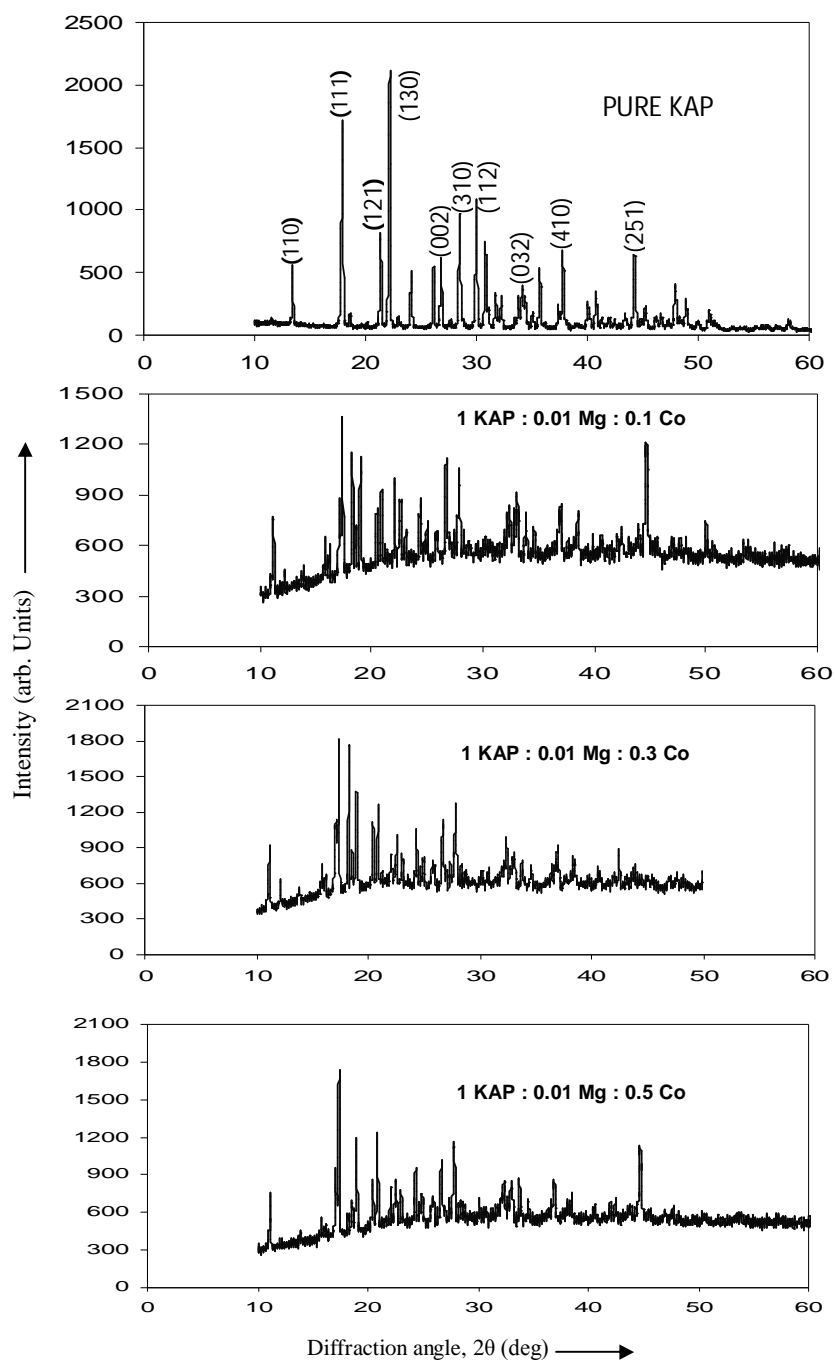


Fig. 3. Powder XRD Spectra of KAP and different molar concentration of CMKAP Crystals.

*X-ray analysis:* Powder XRD patterns were recorded for pure KAP and for different concentration of CMKAP as shown in Fig. 3. The XRD pattern of KAP and CMKAP showed slight shift in the peak position, an indication of incorporation of the dopants. The lattice parameters of pure KAP and bimetallic doped KAP were determined and values are presented in Table 1. It is observed that the lattice parameters and cell volume of bimetallic doped KAP crystals slightly differ from those of pure KAP, which may be attributed to the presence of metal ions dopants in KAP crystals. The XRD results confirm that the incorporation of bimetallic ions into the KAP crystal lattice without changing the basic structure of the crystals.

**Table 1. Unit cell parameters of pure and bimetallic doped KAP crystals.**

Crystals	a (Å)	b (Å)	c (Å)	V (Å <sup>3</sup> )
Pure KAP	9.553	13.243	6.647	840.914
1KAP:0.01Mg:0.1Co	9.097	13.075	6.679	835.434
CMKAP 1KAP:0.01Mg:0.3Co	9.039	13.103	6.683	791.521
1KAP:0.01Mg:0.5Co	9.554	13.134	6.679	838.096

*Differential scanning calorimetric study:* For pure KAP, one broad endothermic peak is observed in the range of temperature 235 to 337°C. This is due to the decomposition of KAP crystal without melting or phase transformation. Hence, the carbon dioxide (CO<sub>2</sub>) and carbon monoxide (CO) are expected to be liberated as volatile fragments from KAP sample. In Fig. 4, the first major endothermic peak around 85 to 165°C is due to the removal of water molecules. There are 7 molecules of water present in magnesium and cobalt sulphate. The 2nd endothermic peak around 225 to 287 °C might be attributed to decomposition of metal ions Mg<sup>2+</sup>. The 3rd endothermic peak around 340 to 375°C matches the onset decomposition of KAP. The slight increment in temperature is evident for the doped crystals suggesting that the substitution of Mg<sup>2+</sup> and Co<sup>2+</sup>. In case of KAP doped with Mg and higher amount of Co (1: 0.01: 0.5), there is a slight reduction in the decomposition temperature found in the range of 331 to 371°C which may be attributed to the decrease of bond energy caused by the addition of higher amount of Co<sup>2+</sup> ions.

*UV-VIS studies:* The UV-VIS spectrum gives limited information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electron in  $\pi$  and  $\sigma$  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. The optical transmission spectra for KAP and various concentration transmission spectra of CMKAP crystals are shown in Fig. 5. Crystals of thickness ~1 mm were used. Pure KAP and colorless doped KAP crystals have sufficient transmissibility in the entire visible region.

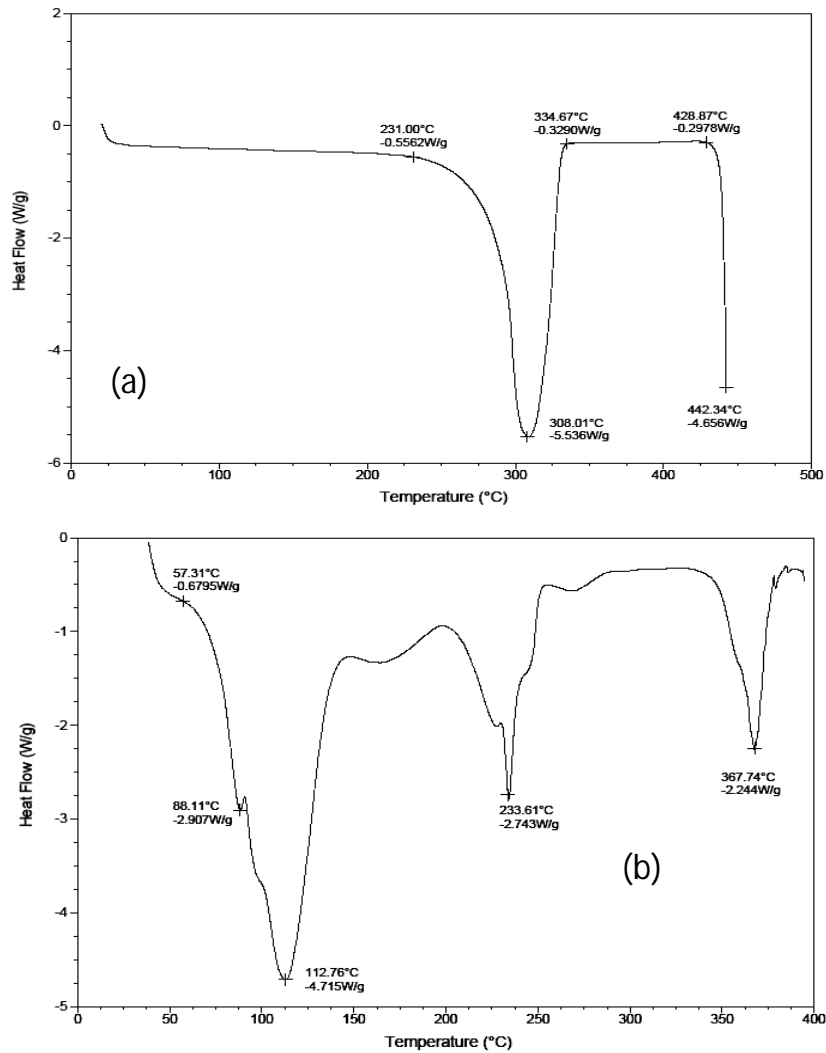


Fig. 4. DSC curve of (a) Pure KAP, (b) KAP doped with 0.01 Mg:0.5 Co crystal.

The good transmission of the crystal in the entire visible region suggests its suitability for second harmonic generation devices. The absorption edge from the grown KAP and doped KAP crystals were observed to be around 300 nm due to the  $n\text{-}\pi$  transition of the carbonyl group of the carboxyl functions. In the case of (1 : 0.01 : 0.1), (1 : 0.01 : 0.3) and (1 : 0.01 : 0.5) doped CMKAP crystals were seen to appreciably modify broad absorption occurred in the visible region and this was due to the color centered in the lattice. The transmission percentages of different bimetallic doped KAP crystals are found to be decreased compared to that of pure KAP.

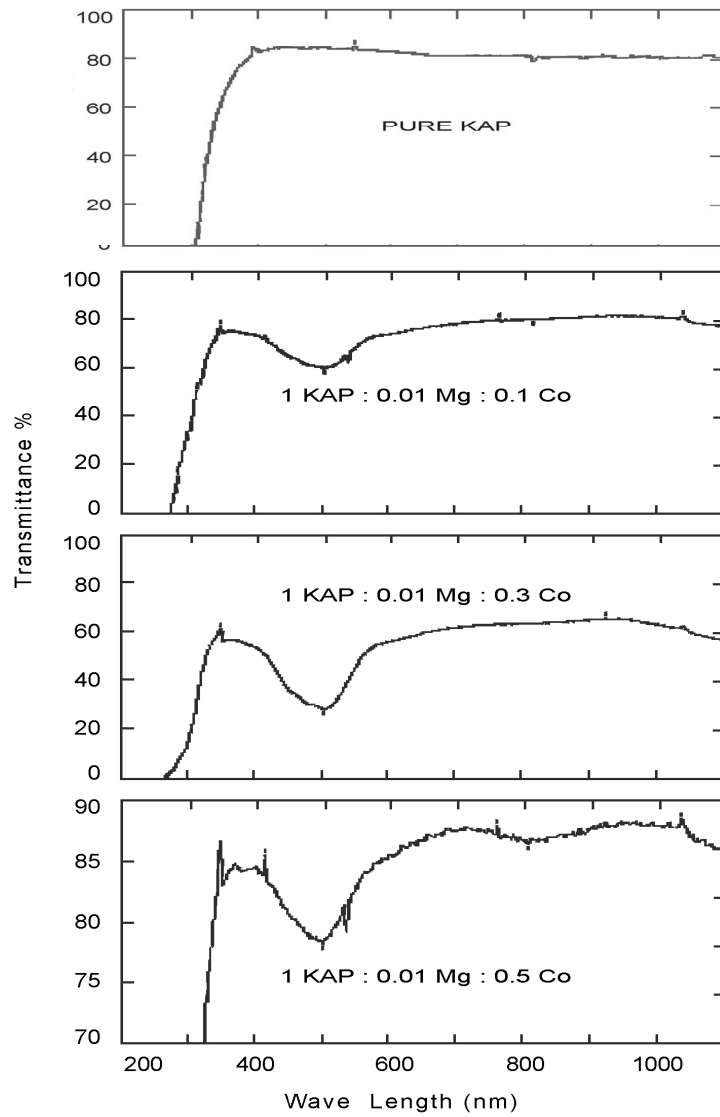


Fig. 5. Transmission spectra of different molar concentration of CMKAP Crystals.

## CONCLUSIONS

The growth of pure KAP and  $\text{Co}^{2+}$ -  $\text{Mg}^{2+}$  bimetallic doped KAP crystals in supersaturated aqueous solutions have been investigated. The effects of bimetallic impurities on KAP solution are found to increase the metastable zonewidth considerably. This may be due to the suppression of chemical activity of the heavy metal ions those are

present as impurities in the KAP solutions. Colouration is observed in cobalt co-doped with magnesium in KAP crystals. This may be due to incorporation of larger sized cations like  $\text{Co}^{2+}$  along with  $\text{Mg}^{2+}$  into the superficial crystal lattice and forming defect centers. This study would be useful to achieve good quality bulk and cloured KAP crystals from aqueous solutions with faster growth rates. The good transmission of the crystal in the entire visible region suggests its suitability for second harmonic generation devices. The powder X-ray diffraction analysis reveals the stable lattice on doping in KAP. The maximum limit of temperature for NLO application of these crystals has been found by thermal analysis.

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