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Review Article

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A comparative study on the effect of Cu, Pd, Mg dopant during the growth of KAP single crystals

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ABSTRACT

Synthesis and characterization of good optical and organic single crystals are important among researchers due to its wide range of applications. In this review, we analyzed the synthesis kinetics, structural, thermal, optical and mechanical properties of Mg, Pd and Cu doped potassium acid phthalate (KAP) single crystals. In our previous studies we prepared these metal ions doped KAP single crystals and studied its various physio chemical properties. Here we compared our previous results for better understanding of metal doped KAP single crystals.

Keywords: potassium acid phthalate, slow evaporation method, nonlinear optical properties, mechanical properties.

INTRODUCTION

The development of organic crystals have been intensively concentrated by the researchers due to its large nonlinear optical coefficients, high resistance towards laser induced damage, low angular sensitivity and excellent mechanical properties [1]. Specifically, the non linear property of this organic material got great importance in various optoelectronic devices including LCD and other flat panel displays. Practically, low transparency, moderate mechanical strength and inability to produce large crystal limit the use of organic crystal in modern optoelectronic devices. In addition to this, the organic crystals belonging to orthorhombic system exhibits extraordinary physical properties such that, piezoelectric and ferroelectric property [2]. In this connection various organic crystals have been investigated by the researchers to overcome the above problem. Among them, potassium hydrogen phthalate ($K(C_6H_4COOH–COO)$) single crystal got considerable attention because of its interesting pyroelectric, elastic, piezoelectric and non linear optical properties. This potassium hydrogen phthalate (KHP) or potassium hydrogen phthalate (KAP) also belongs to orthorhombic crystal system with space group of Pca21 with the corresponding lattice parameters are a = 9.605 Å b = 13.331 Å c = 6.473Å and $\alpha = \beta = \gamma = 90°$ [3]. The platelet morphology with the perfect cleavage at (010) plane of KAP makes a suitable substrate for the growth of higly oriented conjugated polymers along good non linear property. This alkali acid KAP single crystal exhibits exceptional physical and chemical properties. Furthermore, this KAP crystal widely used as the second, third and fourth harmonic generator for lasers operations, specially Nd: YAG and Nd: YLF lasers [4].

A large number of technique such as, slow evaporation technique, floating seed technique, sol gel technique, slow cooling technique and etc. have been adopted by the researchers to obtain high quality KAP single crystals. Among them slow evaporation technique is a suitable technique for the growth of large size KAP single crystals [5]. Moreover, this simple, efficient, and low cost process results extraordinary physical and chemical properties and showing good application prospect for higher order harmonic generations. Anyhow, doping is necessary to further

increase the transparency and mechanical strength of KAP single crystals. Researchers have been believed the addition of transition metal ions highly influence the growth kinetics of KAP single crystals. According to this, various bivalent and trivalent transition metal ions such that Fe^{3+}, Cr^{3+}, Zn^{2+}, Mg^{2+} and etc were doped with the KAP single crystals [6]. As a result, this kind of metal ion doping induces the significant changes in the properties of potassium acid phthalate single crystals.

In our pervious study, we synthesized Mg, Pd and Cu transition metal ions doped KAP single crystal and studied its structural, optical and mechanical properties. So, it is necessary to compare the effect of Mg, Pd and Cu dopant on KAP single crystal. Thus, In this communication, we reviewed the synthesis process, structural, thermal, optical and mechanical properties of Mg, Pd and Cu doped KAP single crystals.

Synthesis of KAP Single crystal:

Potassium acid phthalate (KAP) single crystal was synthesized by the slow evaporation solution growth technique in atmospheric conditions. First the appropriate amount of KAP dissolved in double distilled water to obtain saturated solution and filtered using microfilter paper of 0.1 µm. Then the recrystallization process was carried out to eliminate the impurities in the KAP crystal. The divalent dopants Mg^{2+}, Pd^{2+} and Cu^{2+} ions were selected as dopant in the form of $MgCl_2$, $PdCl_2$ and $CuCl_2$ respectively. During the doping process we varied the metal ion concentration form 0.1 to 0.3 mol%. Then the corresponding metal chloride solution was added to the saturated KAP and well stirred and stored in separate beakers. We maintained the pH value 4 all solution and the final solution covered with perforated sheets. Finally, the seed crystals were allowed to float on the surface of the saturated solution and left for slow evaporation at room temperature. The single crystal of KAP was formed at the end of 4 days by evaporation of solvent. The grown KAP single crystals were harvested and used for further characterization studies. The photograph of Mg^{2+}, Pd^{2+} and Cu^{2+} ions doped KAP single crystal is shown in Fig.1.

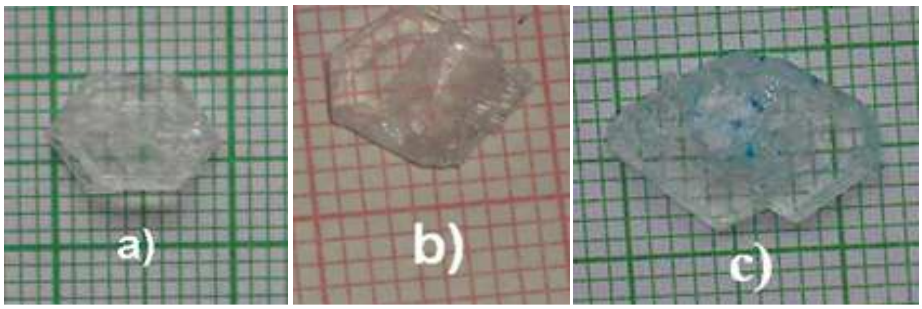

Fig. 1. Photographs of 0.1 mol% Mg^{2+}, Pd^{2+} and Cu^{2+} ions doped KAP single crystal

Structural Property:

The structural property of the pure and Mg^{2+}, Pd^{2+} and Cu^{2+} ions doped KAP single crystal were studied by Powder X-Ray diffraction technique. In this work we have used Joel JDX 8030 Powder X-Ray diffractometer with CuKα1 wavelength 1.5406 Å. Our XRD results confirmed that the synthesized pure and Mg^{2+}, Pd^{2+} and Cu^{2+} ions doped KAP single crystal exhibits orthorhombic crystal systems with the space group of $Pca2_1$. In addition with this, all XRD patterns were good agreement with the JCPDS data 31-1855. The addition of transition metal ion dopant didn't alter the peak position but a significant change was observed. This is not surprise because the atomic radii of Mg^{2+}, Pd^{2+} and Cu^{2+} ions are 0.86 Å, 0. 88 Å and 0. 52 Å respectively, which is very small compared to the atomic radii of potassium (1. 52 Å). Thus the addition of metal ions simply decreases the intensity of XRD patterns without changing the crystalline matrix of KAP [7].

Thermal Property:

The thermal stability and purity of synthesized pure and Mg^{2+}, Pd^{2+} and Cu^{2+} ions doped KAP single crystal were studied by thermogravimetric analysis. In this work we have used Universal V4.3A TA instrument (SDT Q600 V8.3 Build 101) with the heating rate of 20°C/min. Thermo gravimetric analysis (TGA) was carried out in air atmosphere between the temperatures of 30 to 1000°C. From the weight analysis we observed that the experimentally observed weight loss at various stages is well agreed with the theoretically calculated values. In all the cases, we didn't absorb any weight loss below 250°C indicates the absence of physically adsorbed water molecules. When the temperature increased from 250°C the decomposition of KAP begins and total 40% of weight loss was observed in all cases. In

addition, an endothermic peak was observed at ~310-320°C in all metal ions dope KAP single crystals which is little bit higher than the endothermic peak at ~300°C of pure/undoped KAP single crystal. Thus the presence of transition metal ion in KAP crystal was confirmed by Thermo gravimetric analysis. The thermo gravimetric analysis of metal ion doped KAP crystal is shown in Fig.2.

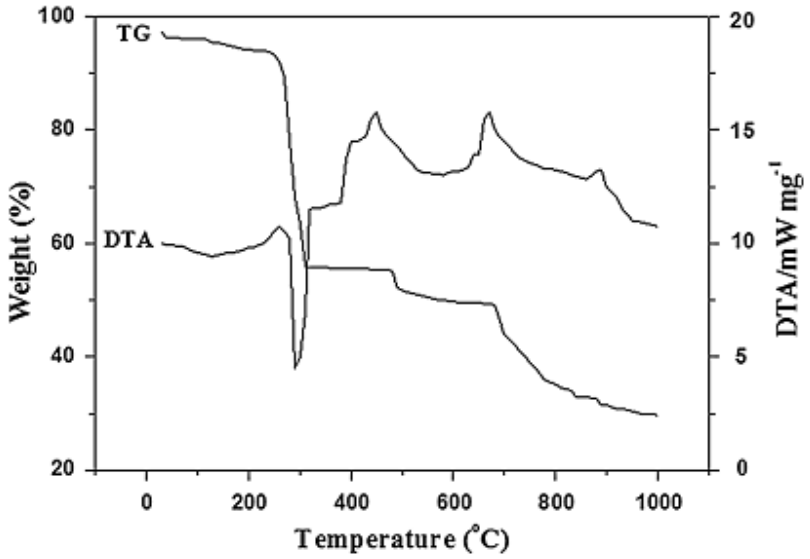

Fig.2. Thermo gravimetric analysis of metal ion doped KAP crystal

Optical Property:

UV–Visible spectroscopy technique is an efficient tool to determine the optical property of the KAP single crystals and it is an important property for a material to be optically active [8]. During the analysis, pure and transition metal ion (0.1, 0.2 & 0.3 mol %) doped KAP single crystal were placed in the crystal holder and 190-1000 nm wavelength UV-NIR radiation was allowed to pass through the (0 1 0) face of grown crystals. The pure KAP single crystal exhibits high optical transmittance about >55% which is higher than all other transition metal ion doped KAP single crystals. For instance, Mg^{2+}, Pd^{2+} and Cu^{2+} ions doped KAP single crystals exhibits 35-55%, 35-55% and 30-55% transmittance respectively. The observed decrement in transmittance conformed the doping of divalent Mg, Pd and Cu ions into KAP. We also studied the FTIR spectroscopy to conform the chemical composition of all corresponding functional groups.

Mechanical Property:

It is important to study the mechanical property of the synthesized pure and Mg^{2+}, Pd^{2+} and Cu^{2+} ions doped KAP single crystals for destructive applications. Hardness technique is the best useful nondestructive technique to determine the harness property of the single crystals [9]. In our work we have used Vickers micro hardness test on pure and Mg, Pd and Cu doped KAP single crystals. The micro hardness tester flitted with a diamond indenter and the indentation was made for various loads from 25, 50 and 100g. Finally, we have calculate the micro hardness values by using the formula $Hv = 1.8544\ P/d^2\ kg/mm^2$, where Hv is the Vickers micro hardness number, P is the applied load (kg) and d is average diagonal length of the indentation (nm) [10]. The addition of metal ion concentration from 0.1 mol% to 0.3 mol% gradually increased the hardness of the KAP single crystals. The same tend was observed in all transition metal ion doped potassium acid phthalate single crystals. The 0.3 mol% of Mg, Pd and Cu ions exhibits high Vickers hardness value and the corresponding values are 130, 92 and 125 kg/mm^2 respectively.

CONCLUSION

In this review, we analyzed the synthesis process, structural, thermal, optical and mechanical properties of Mg, Pd and Cu doped KAP single crystals. All the characterization studies we confirmed that the addition of transition metal ions highly influence the properties of pure KAP single crystals. But, the XRD pattern confirms even at high molar concentrations the metals ions didn't alter the crystalline structure of KAP crystal. The optical property and thermo

gravimetric analysis also confirmed the presence of Mg, Pd and Cu ions and its influence in respective properties. Thus, the addition of Mg^{2+}, Pd^{2+} and Cu^{2+} ions results significant changes in the pure KAP single crystals.

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