

RESEARCH ARTICLE

Concentration of crystal violet dye on the growth, optical, photoluminescence and laser damage threshold properties of potassium acid phthalate single crystal

G. Babu Rao, P. Rajesh* P. Ramasamy

Crystal Growth Lab, Department of Physics, SSN College of Engineering, Kalavakkam-603110, Tamil Nadu, India

Received 8 August 2015; Accepted 30 October 2015 Available online 30 October 2015

Abstract

Influence of crystal violet dye with different ratio (0.1 mol%,0.3 mol% and 0.5 mol%) on potassium acid phthalate single crystal by conventional method has been studied. Dye inclusion crystals have attracted researchers in the context of crystal growth for applications in solid state lasers. The grown crystal is subjected to optical, photoluminescence and laser damage study to explore its suitability for the solid state dye laser applications.

Introduction

The potassium salt of phthalic acid, namely potassium acid phthalate (KAP), with chemical formula $C_8H_5O_4K$, it crystallized into the orthorhombic form with four molecules per unit cell. KAP crystals have excellent physical properties and have a good record for long term stability in devices [1-3]. It exhibit piezoelectric, pyroelectric, ferroelectric, elastic and nonlinear optical properties [4]. Monica Enculescu [5] has studied the effect of rhodamine 6G, coumarine 6 and polyvinylpyrrolidone (PVP) on KAP crystals using solution growth method. It was reported that the dopants enhance the second harmonic generation (SHG) efficiency of KAP. Dye

*Corresponding author:Tel: +91- 9445434893. Fax: +91 9840522490,

E-mail: rajeshp@ssn.edu.in

Published by GM SOFTWARE

Keywords

Growth from solutions X-ray diffraction Optical properties Non-linear Optical crystal

inclusion crystals have been investigated in the context of many areas ranging from crystal growth to solid state lasers. Thus second harmonic generation of Nd-YAG laser light is suitable for pumping the dyes in order to achieve lasing effect [6-7].

Experimental

Saturated solution of pure KAP is obtained by dissolving potassium hydrogen phthalate in the double distilled water (18.2 M Ω m resistivity). The saturated solution of KAP is divided into four different beakers. The beakers contains pure different ratio (0.1 mol%, 0.3 mol% and 0.5 mol %) of crystal violet (CV) added solution. It is continuously stirrer for 4 h using magnetic stirrer for homogenization. The filtered solution kept for slow evaporation at room temperature. After 25 days, bluish transparent crystals with average dimension of 10 x 6 x 3 mm³ are harvested. The grown crystals are shown in the **Fig 1**. It is observed that in the 0.1 mol% dye doped crystal dye molecules are equally distributed and when

concentration of the dopant is increased to 0.5 mol% the distribution of dye molecule is not equal. This may be due to the fact that dimers are formed at higher concentration of the dye [8].



Fig 1 Grown crystals of a) Pure KAP b) 0.1 mol% CV doped Kap c) 0.3 mol % CV doped KAP and d) 0.5 mol% CV doped KAP

Results and discussion

Powder X-ray diffraction

Powder form of the pure and different molar ratio of CV added KAP single crystal was taken for the powder XRD using X'Pert pro panalytical diffractometer using nickel-filtered Cu-Ka radiation (0.15418 nm) as source and operated at 40 kV and 30 mA. The indexed powder XRD pattern of the grown crystal is shown in Fig 2. The obtained 2θ values are used for indexing using the 'TWOTHETA' software package. The well defined and sharp peaks signify the good crystalline nature of the compound, and the intensity of the peak is varied by increasing the concentration of the dopant. Powder XRD results show that the doped crystal retains its original structure and it reveals that the dopant does not affect the structure of pure KAP.



Fig 2 Powder XRD of pure and dye doped KAP single crystals

UV-Vis NIR analysis

UV-Vis transmittance spectra were recorded for the grown crystals with 2 mm thickness using Perkin Elmer UV-Vis –NIR Spectrophotometer in the range between 200 and 1100 nm. The observed spectrum is shown in fig 3, there is no absorption in the range 300–1100 nm for pure KAP crystal. A prominent characteristic absorption edge is observed at 300 nm in all the cases. In the case of dye-doped KAP crystals, a broad absorption peak between 450 and 650 nm has been observed. The higher transmittance in the near IR region for 0.1 mol% CV doped crystal compared to the pure KAP, 0.3 mol% and 0.5 mol% doped KAP crystals.



Fig 3 UV Visible analysis for the grown crystals

Photoluminescence study

Photoluminescence is carried out using Shimadzu Spectrofluorophotometer RF-5031 PC Series in with the slit width of 3 nm at room temperature. The powder sample of pure and different concentration of crystal violet dye doped KAP single crystals were excited at 440 nm and the emission spectrum were recorded between 500 nm to 800 nm and observed spectra are shown in **Fig 4**.



Fig 4 Photoluminescence study for the grown crystals

From the **Fig 4**, it is observed that pure KAP has no emission and 0.1 mol% CV doped KAP shows the emission at 638 nm with high intensity peak. In the case of 0.3 mol% CV doped KAP the emission was observed at 648 nm .The 0.5 mol% CV doped KAP shows the very weak peak at 640 nm due to unequal distribution of dye.

Laser damage threshold

Like other optical materials used in laser technology, NLO crystals are susceptible to optically induced catastrophic damage. From this view point, we carried out laser damage threshold measurements on the grown crystals. The similar KAP samples (pure, 0.1 mol%, 0.3 mol% and 0.5 mol% CV added KAP) were prepared for laser damage threshold studies with 2 mm thickness. A Nd: YAG laser with pulse width of 7ns and 10Hz repetition rate was passed along the (010) face for all the crystals. The beam was passed along the (010) direction for all the crystals. Initially 6 mJ was applied on the surface of the pure KAP crystal for 20 seconds, no damage was observed. Experiment is repeated with 12 mJ of energy, within 5 seconds the damage was observed. For 0.1 mol% of CV added KAP with 6 mJ of energy for 20 seconds no damage is observed, but with 12 mJ of energy the crystal withstands upto 8 seconds, after that a small dot is observed on the cleavage. For 0.3 mol% of CV added KAP crystal 6 mJ of energy is passed and a small dot is formed in 10 seconds, experiment is repeated with 12 mJ of energy and a crack is formed in 10 seconds. In the case of 0.5 mol% CV added KAP with 6 mJ of energy in 10 seconds a dot is formed on the surface of the crystal and after increasing the energy to 12mJ in 10 seconds crack is formed on the crystal. Due to the equal distribution of dye in the 0.1 mol % CV added KAP it shows the higher stability for higher energy compared to 0.3 and 0.5 mol % CV added KAP.

Conclusions

Crystal violet dye with different ratio was successfully doped in KAP and the dopant influenced the optical, photoluminescence and lesar damage threshold properties of KAP. The dye doped crystals strong absorption in the visible region and high transmittance in the near IR region, and is very good candidate for optical applications. The high luminescence emission intensity in the dye doped crystal shows the good crystalline nature as result of dye doping. The laser damage study shows the high concentrated dye doped crystals are withstands for the high energies.

References

- [1] L. Beck, P. Stemmler, F. Legrand, *Rev. Sci. Instr.*, 66, (1995), 1601.
- [2] B. Jason, Benedict, P. M. Wallace, P.J. Reid, S. Jang, B. Kahr, *Adv. Mater*, (2003).
- [3] N. Kejalakshmy, K. Srinivasan, J. Phys. D: Appl. Phys., 36, (2003), 1778.
- [4] A. E. Kumaran, P. Kanchana, C. Sekar, *Spectrochm. Act A*, 91, (2012), 370.
- [5] M. Enculescu, *Physica B*, 405, (2010), 3722.
- [6] B. Raju, A. Saritha, G. Bhagavannarayana, K. A Hussain J. Cryst. Growth, 310, (2008), 4143.
- I. Pritula, V. Gayvoronsky, Yu. Gromov, M. Kopylovsky, M. Kolybaeva, V. Puzikov, A. Kosinova Yu.Savvin, Y. Velikhov, A. Levchenko, *Optics Comm.*, 282, (2009), 141
- [8] J. Kunzler, L. Samha, R. Zhang H. Samha, Am. J. Res., 9, (2011), 1.