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Characterization of potassium bromide crystals grown in the aqueous solution of picric acid

J. Uma Maheswari [a,*], C. Krishnan [b], S. Kalyanaraman [c], P. Selvarajan [d]

[a] Department of Physics, The M.D.T.Hindu College, Tirunelveli 627010, Tamilnadu, India
[b] Department of Physics, Arignar Anna College, Aralvoymoli 629301, Tamilnadu, India
[c] Physics Research Centre, Sri Paramakalyani College, Alwarkurichi 627412, Tamilnadu, India
[d] Department of Physics, Aditanar College of Arts and Science, Tiruchendur 628216, Tamilnadu, India

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ABSTRACT

Potassium bromide crystals were grown in the aqueous solution of picric acid by slow evaporation technique at room temperature. X-ray Diffraction (XRD) analysis ensures that the grown sample is in *Fm3m* space group and FCC structure. Energy Dispersive X-ray Spectroscopy (EDX) reveals the presence of elements in the title compound. UV–Vis-NIR spectrum reveals that the grown sample is a promising nonlinear optical (NLO) material. FTIR analysis confirms the functional groups present in the sample. The thermogravimetric (TG) and differential thermogravimetric (DTA) analyses ensure that the sample material is thermally stable up to 160 °C. The second harmonic efficiency of the sample is 1.3 times greater than that of standard KDP. The mechanical strength of the grown sample is estimated by Vickers microhardness tester. The electrical properties were investigated by impedance analysis and the results of various studies of the grown crystals are discussed.

1. Introduction

Materials having large nonlinear optical properties and excellent thermal and mechanical properties were not sufficient for the advanced photonic technology and this leads to invention of new category of materials viz. semiorganic NLO materials. The lack of extended π - electron delocalization causes relatively modest nonlinearity in pure inorganic materials even though having excellent mechanical and thermal stability over organic materials [1,2]. The large nonlinearity, high resistance to laser induced damage, good mechanical strength and low angular sensitivity [3] of semiorganic materials attracted the current research in science. The present study emphasis on potassium bromide single crystals grown in the aqueous solution of picric acid (PBP[1]) that combines the advantages of organic and inorganic materials. From the literature survey, it is observed that the growth and characterization of some nonlinear optical materials such as L-histidinium chloroacetate [4], lithium nitrate monohydrate oxalate [5], γ-glycine crystal grown from potassium bromide [6], L-leucine hydrobromide [7] were reported.

L-alanine L-alaninium picrate [8], L-Leucine L-Leucinium picrate [9], 2-aminopyridinium picrate (2APP) [10], L-tryptophanium picrate [11] are some of the reported crystalline picrates formed from picric acid. In biological and bioelectrical systems picric acid complexes used as an anti fungal and anti bacterial agents. Moreover, the picric acid complexes mostly encourages the acentric packing which results enhanced hyperpolarizability (β) and second order NLO activity χ^2 [12]. The crystalline picrates of various organic molecules were produced by picric acid through ionic and hydrogen bonding and π–π interactions [13]. In spite of high transmittance KBr is found to be inactive in second harmonic generation (SHG) efficiency. So in the present investigation, crystals of potassium bromide are grown in the aqueous solution of picric acid to explore the SHG efficiency. The material PBP was grown successfully and found to have good NLO behavior and is a π donor–acceptor molecular compound where potassium bromide acts as a donor and picric acid as an acceptor. The asymmetric unit of PBP crystal contains a potassium cation and a picrate anion, where the carboxyl group is protonated. Thus in the carboxyl group a π–π^* transition occurs and which rises nonlinear properties [14] of the title compound remarkably. The grown PBP crystals were characterized by various studies such as XRD, FTIR, transmittance, EDX – SEM, NLO, thermal, mechanical and dielectric studies.

* Corresponding author.
E-mail address: umak.anand@gmail.com (J.U. Maheswari).
[1] Potassium bromide crystal grown in the aqueous solution of picric acid.

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2. Crystal growth

Analytical grade potassium bromide (NICE-India) and picric acid (HIMEDIA-India) were mixed in stoichiometric ratio 1:1 in double distilled water. The supersaturated solution with pH value of 5 was stirred continuously through 2 h and filtered using Whatmann filter paper and set to slow evaporation at room temperature. Over a period of 25 days, different sized single crystals with good optical qualities were harvested. The grown crystals of PBP are shown in Fig. 1. The dimension of the biggest grown crystal shown in the photograph is $15 \times 12 \times 6\ mm^3$.

3. Material characterization techniques

Single crystal X-ray diffraction (SCXRD) studies of the grown sample were carried out by Enraf Nonius CAD4-MV31 single crystal X-ray diffractometer. The unit cell parameter, space group were also determined. The result of SCXRD was confirmed by powder X-ray diffraction using PANalytical X′pert Pro powder X′ celerator Diffractometer in the range 10–80° in 2θ. The optical properties of the title compound were studied using UV–Vis–NIR spectrophotometer (Varian, Cary 5000) in the range 190–1100 nm. FTIR spectrum was recorded using Perkin Elmer spectrometer in the range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} by the KBr pellet technique. The composite elements of the title compound material were estimated by Energy Dispersive X-ray spectroscopy (EDX) and Scanning Electron Microscopy (SEM) image of the crystal also recorded using Make – JEOL Model – JSM 6390. The thermogravimetric (TG) and differential thermo gravimetric (DTA) studies were done for the grown sample using Perkin Elmer Thermal analyzer at a heating rate from 40 °C to 730 °C at 20 °C/min. Nonlinear optical properties of PBP were tested by Kurtz Perry Powder technique using a Q-switched high energy Nd: YAG laser (Quanta Ray model Lab-170-10) with λ=1064 nm. The impedance and electric behavior of the sample were studied by an impedance analyzer model: ZAHNER/Germany–electro chemical work station.

4. Result and discussion

4.1. XRD Studies

4.1.1. Single crystal XRD method

The grown crystal was subjected to single crystal X-ray diffraction (SCXRD) with CuKα radiation (λ=1.5406 Å) to reveal the crystal structure. The grown crystal is in cubic structure with

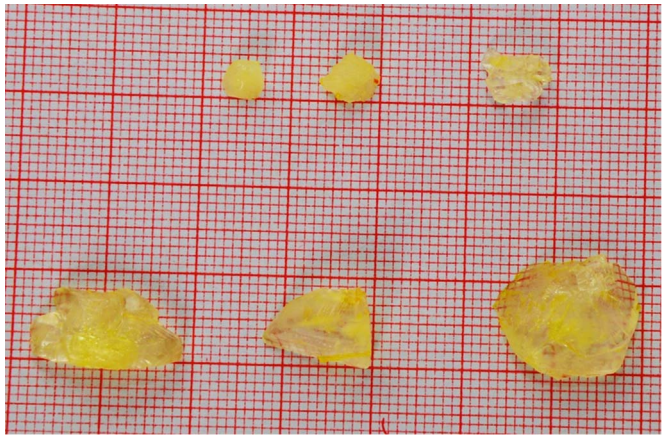

Fig. 1. The grown PBP single crystals.

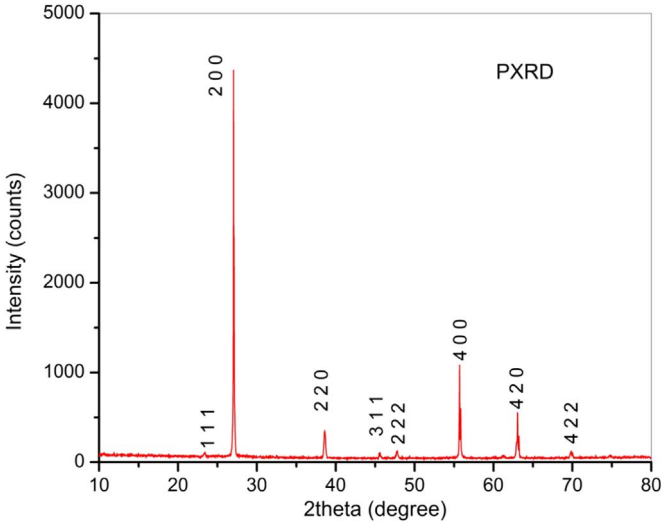

Fig. 2. The Powder XRD pattern of PBP crystal.

lattice parameters a=b=c=6.59 Å, α=β=γ=90° and volume V=286 $Å^3$ with space group *Fm*3*m*.

4.1.2. Powder X-ray diffraction

The powder X-ray diffraction was carried out for the powdered sample of grown PBP crystal with CuK_α (λ=1.5406 Å) radiation from 10° to 80° at a scan rate of 3°/s. Every crystalline substance produces its own XRD pattern, the powder X-ray diffraction pattern of grown material is shown in Fig. 2, which represents only few peaks since the grown crystal has highest symmetry. The observed diffraction peaks are at angle (2θ) of 23.361, 27.039, 38.611, 45.619, 47.770, 55.750, 63.031 and 69.867 which correspond to reflections from (111), (200), (220), (311), (222), (400), (420) and (422) planes of the cubic *Fm*3*m* potassium bromide structure and all are indexed using INDEXING and TREOR softwares. Since the *hkl* mixed odd or even reflections were forbidden, all observed were only in *hkl* odd or even. UNITCELL software ensures the crystal structure, cell parameters and volume obtained from SCXRD.

4.2. Elemental composition study

Quantitative identification of elements with higher atomic numbers in the grown sample is done by EDX and the recorded spectrum of PBP crystal is shown in Fig. 3. The EDX analysis confirms the composite elements in the sample. The carbon, oxygen, potassium and bromine elemental percentage is given in Table 1. The scanning electron microscopic image is depicted in Fig. 4 which shows homogeneous and uniform distribution of grains in the entire surface of title compound.

4.3. UV–Vis-NIR study

The UV–Vis-NIR spectrum is shown in Fig. 5 and the cut-off wave length is found to be at 517 nm. If the sample material PBP is fit for phase matching conditions then it will be used for second harmonic generation application for a 1064 nm laser, since it has wide transparency cut off wavelength. The absorbance at 251 nm is due to π–π^* transition. The delocalization of π electron is responsible for grown crystal's nonlinear optical response and absorption in the UV region [15]. Comparing with earlier reported papers [16–18] and with L-valinium picrate crystal [19] grown by conventional solution growth (SEST) method, the PBP crystal has a fine transmission as desired from UV–Vis region to near IR region.