Optics & Laser Technology 72 (2015) 108–115

Contents lists available at ScienceDirect

Optics & Laser Technology

journal homepage: www.elsevier.com/locate/optlastec

Effect of amino acid dopants on the spectral, optical, mechanical and thermal properties of potassium acid phthalate crystals for possible optoelectronic and frequency doubling applications

J. Thomas Joseph Prakash [a,*], J. Martin Sam Gnanaraj [b], S. Shek Dhavud [c], S. Ekadevasena [b]

[a] Department of Physics, Government Arts College (Affiliated to Bharathidasan University), Trichy 620022, Tamil Nadu, India
[b] PG and Research Department of Physics, H.H. The Rajah's College (Affiliated to Bharathidasan University), Pudukkottai 622001, Tamil Nadu, India
[c] PG and Research Department of Physics, Jamal Mohamed College (Affiliated to Bharathidasan University), Trichy 620020, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 31 December 2014
Received in revised form
25 February 2015
Accepted 31 March 2015
Available online 21 April 2015

Keywords:
Optical materials
Nonlinear optics
Semiorganic

ABSTRACT

Undoped and amino acid (L-Arginine and L-Valine) doped KAP crystals were grown by slow evaporation solution growth technique. The changes in the structural, spectral, optical, mechanical and thermal properties were observed. The sharp prominent peaks in the indexed powder XRD pattern confirms the crystalline nature of the sample. Optical studies reveal that the crystal is transparent in the entire visible light region. Thermal stability was checked by TG/DTA analysis. The mechanical stability was evaluated from Vicker's microhardness test. The SHG efficiency for the title materials was tested with different particle sizes by the Kurtz and Perry powder method, which established the existence of phase matching.

1. Introduction

Potassium acid phthalate (KAP) is a biaxial semiorganic material that crystallises in orthorhombic symmetry and is widely used in X-ray monochromators and X-ray analysers [1–4]. KAP is a pseudo-hexagonal shaped crystal exhibiting orthorhombic symmetry [5]. KAP crystal possesses platelet morphology with a perfect cleavage along the (010) plane [6,7]. It shows interesting piezoelectric, elastic and electro-optical properties. KAP crystals play a prominent role in the field of nonlinear optics [8,9].

Doping amino acid into the crystal lattice of KAP may perform modification in its properties. Amino acids contain chiral carbon atoms that are responsible for the non-centrosymmetric behaviour of the crystals. The hardness property of the crystal is favoured by the presence of zwitter ions [10–16]. Modification of the structural, optical and mechanical properties of KAP crystals by the addition of organic, inorganic and semiorganic impurities were reported by Murugakoothan et al. [10]. A number of researchers reported the structural, optical and habit modification of KAP crystals due to the addition of bivalent metal ions as impurities [17]. The change in the growth and physical properties of KAP crystals was studied by Elakkina kumaran et al. [18]. In this work three amino acids were used as dopants viz., glycine, tyrosine and L-Alanine. Of the three amino acids, L-Alanine possessed better optical property than the other two additives. It was reported that KAP crystals grown by the Sankaranarayanan Ramasamy method and dye doped KAP crystals exhibits excellent optical properties [19,20]. The effect of doping a rare earth ion (Sm^{+}) with KAP crystals was reported by Sudhahar et al. [21]. Baraniraj and Philominathan reported that glycine doped KAP crystals possess better optical, mechanical and thermal properties than undoped KAP [22].

In the present work, we report the variation of structural, spectral, optical, thermal and mechanical properties in the title materials due to amino acid doping. The addition of amino acids tailors various properties of KAP crystals which are very useful in nonlinear optical device applications. Amino acid doped KAP crystals were grown by conventional solution growth technique. For device fabrications, growth of optically good single crystals are essential and so successive recrystallisation was carried out in order to improve the purity of products.

2. Experimental

2.1. Crystal growth

Potassium acid phthalate (Merck, AR grade, 99.8%) L-Valine (Loba, AR grade, 99%) and L-Arginine (Loba, AR grade, 99%) were used as the precursors in the present work. Deionized water was used as a solvent. Calculated amount of KAP was dissolved in deionized water and the solution was stirred at room temperature for about 5 h to get the

* Corresponding author. Tel.: +91 9842470521.
E-mail address: armyjpr1@yahoo.co.in (J.T.J. Prakash).

http://dx.doi.org/10.1016/j.optlastec.2015.03.023
0030-3992/

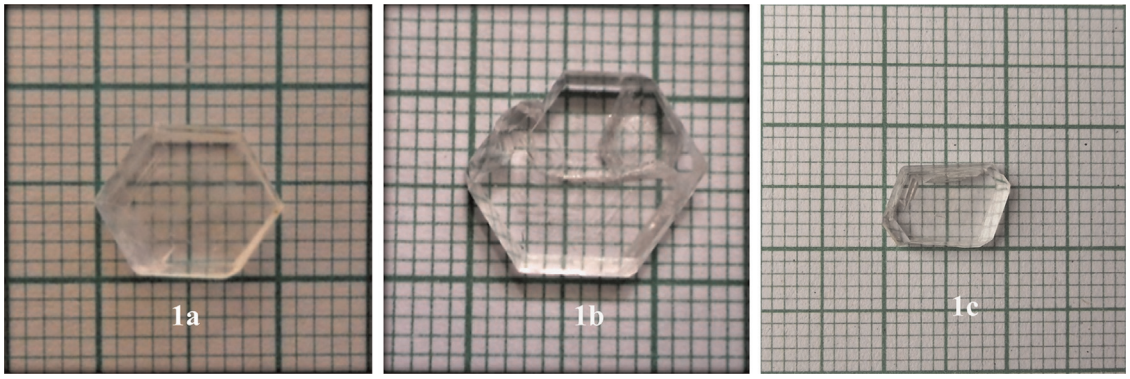

Fig. 1. As grown crystals of (a) undoped (b) L-Arginine doped KAP (c) L-Valine doped KAP crystals.

saturated solution. The solution was filtered in a clean, dry beaker and kept covered in a dust and vibration free zone.

0.1 mol% of L-Valine and L-Arginine was added in the saturated solution of KAP separately. The solutions were continuously agitated for 6 h at room temperature. The clear solutions were filtered in clean beakers and kept in a dust and vibration free atmosphere. Colourless transparent KAP crystals were obtained after period of 20 days. L-Arginine doped KAP crystals were collected after 25 days and L-Valine doped KAP crystals after 27 days. The materials were purified by successive recrystallisation. The photographs of as grown undoped and amino acid doped KAP crystals are shown in the Fig. 1a–c.

2.2. Characterisation techniques

The lattice parameters like length of the unit vectors, interfacial angles, unit cell volume, space group and crystal system were estimated by subjecting the samples to single crystal X-ray diffraction analysis using ENRAF NONIOUS CAD4 X-ray diffractometer. The powder XRD data for the grown crystals were collected using JEOL (JDX-8030) X-ray diffractometer equipped with CuKα radiation. The wavelength of the radiation used was 1.5406 Å. The presence of functional groups, absorption peaks and the tentative bond assignments, nature of the bonds present in the title materials were assessed by FTIR spectral analysis using PERKIN ELMER RXI FTIR spectrophotometer. The optical characters of the samples were examined by subjecting it to linear optical analysis. The absorption and transmission spectrum was obtained within the wavelength range of 190–1100 nm with the help of PERKIN ELMER LAMBDA 35 UV visible spectrophotometer. The thermal stability of undoped and doped KAP crystals was analysed by subjecting it to TG/DTA analysis in a closed chamber with controlled nitrogen flow atmosphere within the range of 50–1200 °C at a heating rate of 20 K/min. Microhardness testing is an important non-destructive technique in order to assess the mechanical stability of the sample. Vicker's microhardness measurements for undoped and amino acid doped KAP single crystals were carried out using Leitz Weitzler hardness tester fitted with a diamond indenter. The Second Harmonic Generation efficiencies of the undoped and amino acid doped KAP crystals were tested by a Q switched Nd:YAG laser (λ=1064 nm) with the input energy 3.2 mJ/pulse and a pulse width of 8 ns.

3. Results and discussion

3.1. Cell parameter estimation

From the single crystal X-ray diffraction results, it was found that both undoped and doped KAP single crystals crystallise in orthorhombic symmetry with a space group of $Pca2_1$. The obtained lattice parameters for undoped and amino acid doped KAP crystals are presented in Table 1. The cell parameters of undoped KAP crystals coincide well with the reported literature [10]. From Table 1 it is evident that the incorporation of dopants does not change the entire structure of doped materials.

Table 1
Lattice parameters of undoped and amino acid doped KAP crystals.

Lattice parameters	KAP reported value [10]	Undoped KAP present work	> L-Arginine doped KAP	> L-Valine doped KAP
a (Å)	6.48	6.56	6.52	6.47
b (Å)	9.61	9.60	9.58	9.59
c (Å)	13.37	13.31	13.27	13.30
α (deg)	90	90	90	90
β (deg)	90	90	90	90
γ (deg)	90	90	90	90
Volume (Å^3)	832	838.21	828.86	825.22
Space group	$Pca2_1$	$Pca2_1$	$Pca2_1$	$Pca2_1$
System	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic

3.2. Crystallinity analysis

The high crystalline nature of the samples was revealed by the prominent peak at specific 2θ angle. The well-defined Bragg's peaks were indexed using JCPDS software (card no: PDF 31-1855). The XRD pattern of undoped and amino acid doped KAP crystal is shown in Fig. 2. The sharpness of the prominent peaks in powder XRD pattern suggests that the title materials are highly crystalline. In the powder XRD pattern of amino acid doped KAP crystals, slight shifts in the prominent peaks are observed. This confirms the addition of dopants into the crystal lattice of KAP crystals. The changes in lattice parameters, due to the addition of amino acids, are responsible for the shifting of prominent peaks. The lattice parameters of the samples were calculated from the equation for orthorhombic system by the method of least squares.

$$\lambda = 2d_{hkl}\sin\theta_{hkl} \quad (1)$$

$$1/d^2 = \left(h^2/a^2\right) + \left(k^2/b^2\right) + \left(l^2/c^2\right) \quad (2)$$

$$V = abc \quad (3)$$

where d is the lattice spacing, hkl are the miller indices, abc are the lattice parameters, λ is the wavelength (CuKα=1.5046 Å), V is the volume of the unit cell and 2θ is the diffraction angle. The lattice parameters calculated from the powder X-ray diffraction is presented in Table 2. From the table it is evident that the crystal retained its orthorhombic structure.