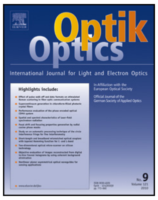
Optik 127 (2016) 3322–3328

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo



Influence of urea doping on optical, thermal, mechanical and electrical properties of L-arginine phosphate monohydrate crystals for NLO applications

Pratik M. Wankhade[a], Anil B. Gambhire[b], Gajanan G. Muley[a,*]

[a] Department of Physics, Sant Gadge Baba Amravati University, Amravati 444602, Maharashtra, India
[b] Department of Chemistry, Shri Anand College, Pathardi, Ahmednagar 414102, Maharashtra, India

ARTICLE INFO

Article history:
Received 4 July 2015
Accepted 5 December 2015

Keywords:
Nonlinear optical material
Electric study
Characterizations

ABSTRACT

In the present investigation, the influence of urea doping on the optical, structural, thermal, mechanical and dielectric properties of L-arginine phosphate monohydrate (LAP) crystal were investigated. Pure and doped LAP crystals were grown from aqueous solution by evaporating solvent at a constant temperature. The presence of dopant was confirmed qualitatively by FT-IR spectroscopy. Powder X-ray diffraction study reveals slight modification in lattice parameters of doped crystal. Ultraviolet–visible–near infrared transmission study reveals increase in optical transparency and band gap of doped crystals with doping concentration. Other optical parameters such as refractive index, extinction coefficient, reflectance, optical and electrical conductivity of pure and doped crystals were evaluated from transmission spectrum only. Noticeable enhancement in second harmonic generation efficiency (1.67 times more) has been observed for 1 mol percent urea doped LAP crystal as compare to pure one. Doped LAP crystals show higher mechanical and thermal stabilities than pure LAP crystal. Electrical properties like as dielectric constant, dielectric loss, ac conductivity and activation energy were also studied.

1. Introduction

An extensive research work has been carried out after the invention of biaxial L-arginine phosphate monohydrate (LAP) crystal in view of its use in nonlinear optical (NLO) applications [1–14]. The SHG efficiency of LAP crystal is three times more than that of famous inorganic potassium dihydrogen phosphate (KDP) crystal [1–3,13]. The low value of dielectric constant of LAP is of special interest in the high-speed electro-optic modulation [14]. Though, LAP is identified as potential NLO material, it suffers from the microbial growth and coloration problem. It constraints the large size growth of crystal. Dhanaraj et al. have solved the problem up to great extent by putting thick layer of n-hexane over the solution and carried out an extensive study on various properties of LAP crystal [5,6]. Doping modify the existing properties upto great extent. On this foot print, an effect of various dopants like thorium, lanthanum, cerium [9] and iodic acid [10] on the physical and chemical properties has also been reported [9,10]. Hameed et al. had studied the ionic interaction with host material by mixing potassium thiocyanate (KSCN) and sodium sulfite in to the LAP crystals [11,12]. An improvement in the optical and thermal properties of urea and thiourea doped LAP crystals has been reported [13].

Urea has large SHG efficiency but its use cannot be materialized in NLO applications due to its poor physical and chemical properties. Muley et al. have studied the growth habit and improvement in the SHG efficiency of KDP crystals doped with urea derivatives [15]. Supriya and Kalainathan have reported the improvement in mechanical properties of urea doped glycine phosphate crystal [16]. In the context of above literature, it is expected that the urea doping may influence thermal, mechanical, SHG efficiency and optical properties of LAP crystal. Although, Premkumar et al. have reported the improvement in thermal stability of LAP due to urea doping but other studies have not been done [13]. In the present investigations, influence of urea doping on the structural, optical, thermal, SHG efficiency, electrical and mechanical properties of LAP crystal has been studied for its effective NLO applications and systematic report is being presented.

2. Materials and method

2.1. Material synthesis and crystal growth

The compound LAP was synthesized by reacting Analar grade L-arginine and phosphoric acid (SD-Fine Chem. India) in equimolar

---

* Corresponding author. Tel.: +91 721 2662279x269; fax: +91 721 2662135.
E-mail address: gajananggm@yahoo.co.in (G.G. Muley).

http://dx.doi.org/10.1016/j.ijleo.2015.12.091
0030-4026/

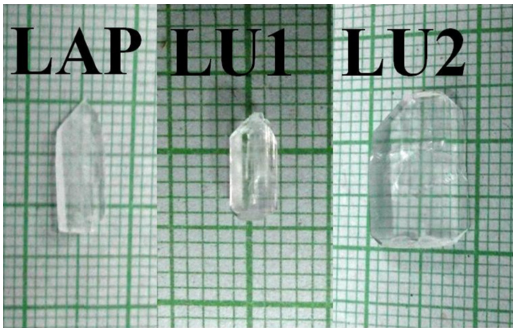


Fig. 1. Photograph of grown crystals.

ratios in double distilled water. The aqueous solution of LAP was stirred on the magnetic stirrer, equipped with hot plate, at a 45 °C temperature for 4 h. The homogeneous solution was filtered using membrane filters assembly and dried optically to get a crystalline compound. The purity of synthesized compound was enhanced by the process of repeatedly re-crystallization from aqueous solution. Crystals of pure LAP and urea doped LAP with different urea concentrations (0.1 and 1 mol percent named as LU1 and LU2, respectively) were grown from aqueous solution by mixing appropriate amount of urea and LAP and adopting slow evaporation of solvent technique at a constant temperature 35 °C. Good quality crystals (Fig. 1) were grown within 15 days.

2.2. Characterizations

The grown crystals were subjected to the linear and nonlinear optical properties, crystal structural, thermal, mechanical, electrical and functional group studies. Powder X-ray diffraction (XRD) data were recorded on Bruker D8-Advance X-ray diffractometer (Germany) in the diffraction angle range $2\theta = 20–80°$ using CuKα radiation of wavelength 1·5406 Å. Fourier transform infrared (FT-IR) spectroscopy was carried out on the instrument FT-IR spectrophotometer (Model-8400S, Shimadzu, Japan) within wavenumber range 400–4000 cm^{-1} to know the functional groups and confirm doping, qualitatively. Optical transmission of the grown crystals in ultraviolet–visible–near infrared (UV–vis–NIR) range was measured with UV–visible–near infrared spectrophotometer (Black-Comet-SR, Stellarnet Inc., USA). The SHG efficiency was measured by Kurtz and Perry powder method [17]. The thermogravimetric and differential thermal analysis (TG-DTA) was carried out on the instrument DTG-60H simultaneous differential thermal analyzer (Shimadzu, Japan) within the temperature range 40–350 °C. Vicker's hardness test was carried out with the help of Future Tech Micro hardness Tester FM-700 hardness tester fitted with diamond indenter. Electrical study was carried out at various frequencies ranges from 1 kHz to 1 MHz using Agilent impedance analyzer (Model-4284A).

3. Results and discussion

3.1. Crystal structure

The powder XRD patterns of pure and doped LAP crystals recorded using powder X-ray diffractometer and indexed using software Powder-X [18] are shown in Fig. 2. The calculated lattice parameters of pure and doped LAP crystals are given in Table 1. LAP crystallizes in the monoclinic crystal system with a non-centrosymmetric space group $P2_1$. The lattice parameters evaluated in the present study are in well agreement with those reported earlier [1,19]. Obviously, LU2 also crystallizes in the same crystal system and space group with slight variation in the lattice parameters. This variation in lattice parameters attribute to the distortion caused locally inside the crystal by inclusion of dopant.

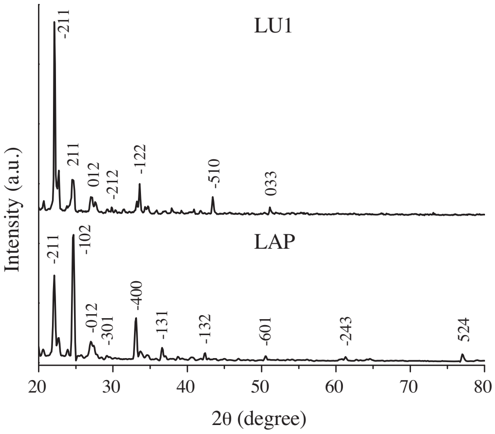


Fig. 2. Powder XRD patterns of pure and doped LAP crystals.

Table 1
Crystallographic data of pure and urea doped LAP crystals.

Crystal	Lattice parameters				
	a (Å)	b (Å)	c (Å)	$\alpha = \gamma$ (°)	β (°)
LAP	10.865	7.911	7.344	90.00	98.09
LU2	10.891	7.919	7.335	90.00	98.01

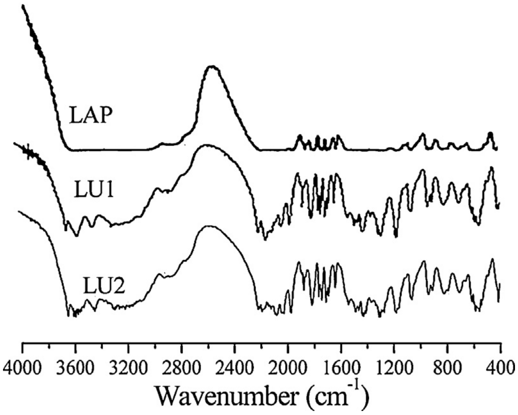


Fig. 3. FT-IR spectra of pure and doped LAP crystals.

3.2. FT-IR spectroscopy

The FT-IR spectra of pure and doped LAP crystals were recorded in the transmission mode within the range 400–4000 cm^{-1} (Fig. 3). The small portion of each crystal was crushed in to the fine powder, mixed separately with KBr and filled in the sample holder to record the spectrum. The peaks assignments are enlisted in Table 2. The broad band of peaks observed in the range 2400–3500 cm^{-1}, corresponds to the symmetric and asymmetric stretching's of NH, CH, and OH bonding. The peak at 499 cm^{-1}, in the pure LAP crystal, corresponds to the P—OH group. The position of this peak is shifted at higher frequency side in the spectra of doped crystals indicating the formation of hydrogen bonding between P—OH group and oxygen of urea molecule. The peak at 1177 cm^{-1} is attributed to the rocking mode of NH_3^+, which is apparent at a same position in doped crystals but another peak at 1213 and 1217 cm^{-1} corresponding to the rocking mode of NH_3^+ group of L-arginine indicates the formation of hydrogen bonding between this group and oxygen atom of urea