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Effect of rare-earth dopants on the growth and structural, optical, electrical and mechanical properties of L-arginine phosphate single crystals

S. Arjunan[a,*], A. Bhaskaran[b], R. Mohan Kumar[c], R. Mohan[c], R. Jayavel[d]

[a] Department of Physics, Sri Ramachandra University, Porur, Chennai, India
[b] Department of Physics, Dr. Ambedkar Government College, Chennai, India
[c] Department of Physics, Presidency College, Chennai, India
[d] Crystal Growth Centre, Anna University, Chennai, India

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ABSTRACT

Effect of Thorium, Lanthanum and Cerium rare-earth ions on the growth and properties of L-arginine phosphate single crystals has been reported. The incorporation of rare-earth dopants into the L-arginine phosphate crystals is confirmed by Inductively Coupled Plasma-Mass Spectroscopy analysis. The unit cell parameters for pure and rare-earth doped L-arginine phosphate crystals have been estimated by powder X-ray diffraction studies. UV–visible studies revealed the transmittance percentage and cut-off wavelengths of the grown crystals. Powder second harmonic generation measurement has been carried out for pure and doped L-arginine phosphate crystals. The dielectric behavior of the grown crystals was analyzed for different frequencies at room temperature. The mechanical properties have been determined for pure and the doped L-arginine phosphate crystals.

1. Introduction

Materials with excellent optical nonlinearities have been studied extensively for their possible applications in optical communication, optical computing, optical information processing, optical disk data storage, laser fusion reactions, laser remote sensing, color display, medical diagnostics, etc [1]. Organic NLO materials are attracting much attention due to their fast and large nonlinear response over a broad frequency range, high optical damage threshold and intrinsic tailorability [2]. The uses of these materials are impended by their poor mechanical and thermal properties. Also it is difficult to grow bulk size optical quality crystals for device applications [3]. Inorganic NLO materials have good chemical stability, high optical quality, excellent mechanical and thermal properties but possess relatively modest optical nonlinearities due to the lack of extended π-electron delocalization [4]. In view of these problems, new types of hybrid NLO materials called semi-organic materials have been explored from organic and inorganic complexes. In these materials, high optical nonlinearity of pure organic compound is combined with the favorable mechanical and thermal properties of inorganic materials [3–6]. Extensive investigation on this direction resulted in the discovery of a new phase-matchable semi-organic NLO crystal, L-arginine phosphate (LAP), which has been proposed as an alternate to potassium dihydrogen orthophosphate (KDP) crystals [7]. The low dielectric constant value of LAP is an added advantage for high-speed electro-optic modulation [8]. It has been reported that the quality and NLO property of LAP crystals can be enhanced with suitable dopants. Improved second harmonic generation efficiency has been observed for the sulphate-mixed LAP and its doped analogs [9]. It has been investigated that the growth of the LAP crystal along the c-axis is suppressed by Cu while it is enhanced by Mg doping [10]. EPR and optical absorption studies of VO^{2+} and Cu^{2+} doped LAP show that the crystal field around these doped ions has rhombic symmetry [11,12]. Large optical power is required to realize the NLO applications for many crystals. Hence, the crystals with high thermal property may play an important role in determining the range of temperatures for a specific application. This requirement has been fulfilled by doping Cu with LAP material [13].

Even though many appreciable changes in the behavior of doped LAP crystals have been reported, there is no report on rare-earth metal ion doped LAP crystal. In this paper, the structural, optical, electrical and mechanical characteristics of Thorium (Th), Lanthanum (La) and Cerium (Ce) doped LAP crystals have been reported.

* Corresponding author. Tel.: +91 9444118583; fax: +91 44 2235 2870.
E-mail address: arjunan_hce@yahoo.co.in (S. Arjunan).

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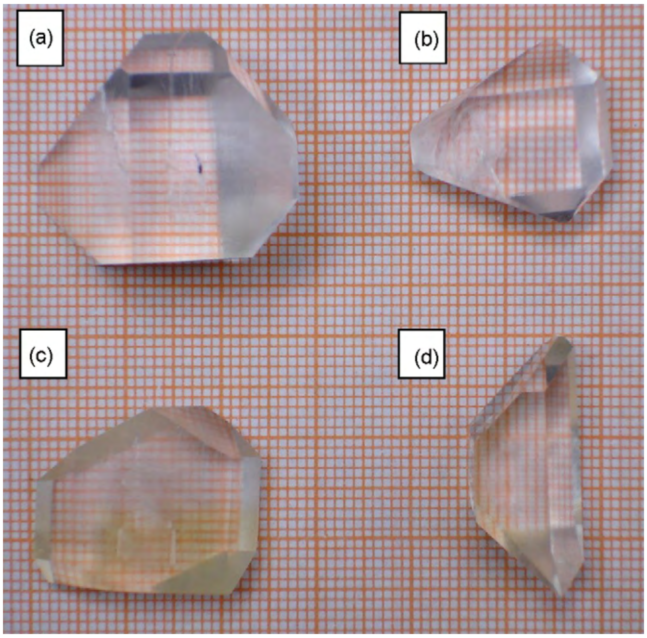

Fig. 1. As-grown single crystals of (a) LAP, (b) ThLAP, (c) LaLAP, and (d) CeLAP.

2. Material synthesis and crystal growth

L-arginine phosphate was synthesized using equimolar ratio of L-arginine and orthophosphoric acid in deionized water based on the following reaction,

$$(NH_2)NHCNH(CH_2)_3CH(NH_2)COOH + H_3PO_4 + H_2O$$
$$\rightarrow (H_2N)_2{}^{+}CNH(CH_2)_3CH(NH_3)^{+}COO^{-}H_2PO_4{\cdot}H_2O$$

The synthesized salt was subjected to repeated recrystallization process in order to improve its purity. A saturated growth solution was prepared from the recrystallized LAP salt and then allowed to evaporate very slowly to obtain optical quality seed crystals. Bulk crystals of LAP were grown by slow cooling technique in a constant temperature bath with a control accuracy of ±0.01 °C, which was achieved by an optical heating arrangement. The growth solution of LAP was maintained at the saturation temperature (42 °C) for 2 days followed by temperature reduction. The solution was initially cooled at a rate of 0.1 °C/day and subsequently 0.2 °C/day as the growth progressed. Bulk LAP crystal grown by slow cooling is shown in Fig. 1(a). One gram of Thorium nitrate, Lanthanum nitrate and Cerium nitrate rare-earth salts were added in LAP solution to grow ThLAP, LaLAP and CeLAP crystals respectively. Bulk crystals of ThLAP, LaLAP and CeLAP were grown as that of pure LAP crystal. The growth parameters were kept constant for all the growth runs. The grown crystals with rare-earth dopants are shown in Fig. 1(b–d).

3. Characterization studies

A RICH-SEIFERT X-ray diffractometer with CuKα radiation (λ = 1.540598 å) was used for powder diffraction analysis. The presence of Thorium, Lanthanum and Cerium metal ion dopants in LAP crystals was confirmed using AGILENT–7500 Ce Series Mass Spectrometer with argon as carrier and make up gas. The optical transmittance spectra of LAP, ThLAP, LaLAP and CeLAP crystals were recorded using CARY 5E UV–VIS–NIR spectrophotometer in the range 185–1000 nm. The SHG output of the grown crystals was measured by Kurtz and Perry powder technique. The dielectric behavior of pure and rare-earth metal ions doped LAP crystals was analyzed for different frequencies at room temperature using HIOKI 3532 50 LCR HITESTER instrument. The Vicker's hardness value of as-grown crystals was estimated at room temperature using MITUTOYO HM 112 microhardness tester fitted with a diamond pyramidal indenter.

4. Results and discussion

4.1. Structural and composition analysis

Powder XRD patterns of pure and Th, La and Ce doped LAP crystals are shown in Fig. 2. The intense and sharp peaks in the diffractogram imply the crystalline perfection of the grown crystals. The unit cell parameters of LAP, ThLAP, LaLAP and CeLAP were estimated using powder XRD data by XRDA programme and the values are presented in Table 1. The calculated cell parameter values are in good agreement with the reported values [14]. Variations in lattice parameters for ThLAP, LaLAP and CeLAP crystals may be attributed to the lattice strain in the grown crystals due to the incorporation of the dopants. The XRD results show that the presence of dopants has not altered the basic structure of the LAP crystal.

The results of ICP-MS analysis show that 72 ppm of Th, 98 ppm of La and 41 ppm of Ce entered into the ThLAP, LaLAP and CeLAP crystals respectively. The amount of dopant ions in the LAP crystal is far below compared to the concentration of the mother solution.

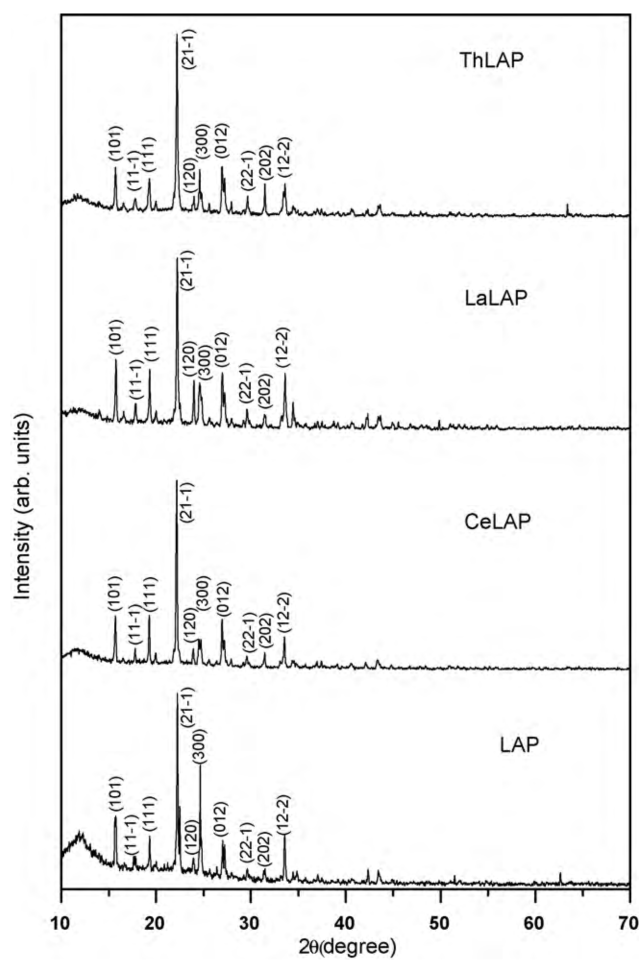

Fig. 2. Powder XRD patterns of LAP, ThLAP, LaLAP and CeLAP crystals. The peaks are indexed for monoclinic structure.