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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

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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.

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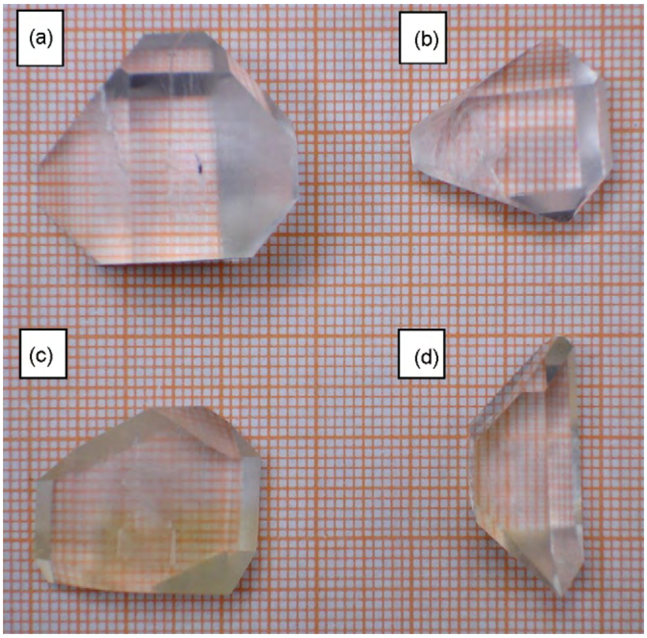

Fig. 1. As-grown single crystals of (a) LAP, (b) ThLAP, (c) LaLAP, and (d) CeLAP.

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.

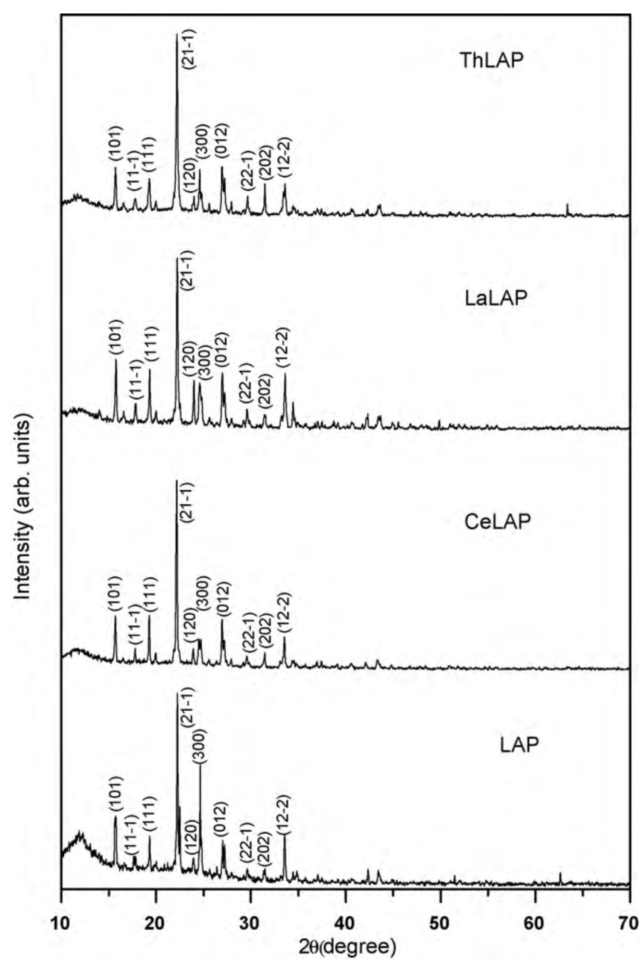

Fig. 2. Powder XRD patterns of LAP, ThLAP, LaLAP and CeLAP crystals. The peaks are indexed for monoclinic structure.

Table 1
Cell parameters of pure and rare-earth doped LAP crystals.

Crystals	*a* (Å)	*b* (Å)	*c* (Å)	*β*°	*V* (Å^3)
LAP (reported) [14]	10.85	7.91	7.32	98.0	628.22
LAP (present study)	10.87 ± 0.0054	7.91 ± 0.0048	7.29 ± 0.0155	98.09 ± 0.06	627.09
ThLAP	10.90 ± 0.0044	7.96 ± 0.0058	7.28 ± 0.0053	98.27 ± 0.05	626.14
LaLAP	10.89 ± 0.0034	7.97 ± 0.0048	7.35 ± 0.0097	97.89 ± 0.02	633.27
CeLAP	10.85 ± 0.0102	7.91 ± 0.0031	7.29 ± 0.0043	98.09 ± 0.03	626.20

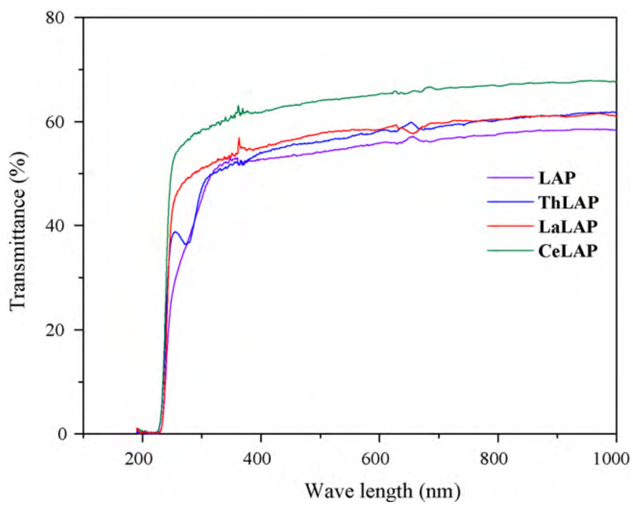

Fig. 3. UV–vis spectra of pure, Th, La and Ce doped LAP crystals.

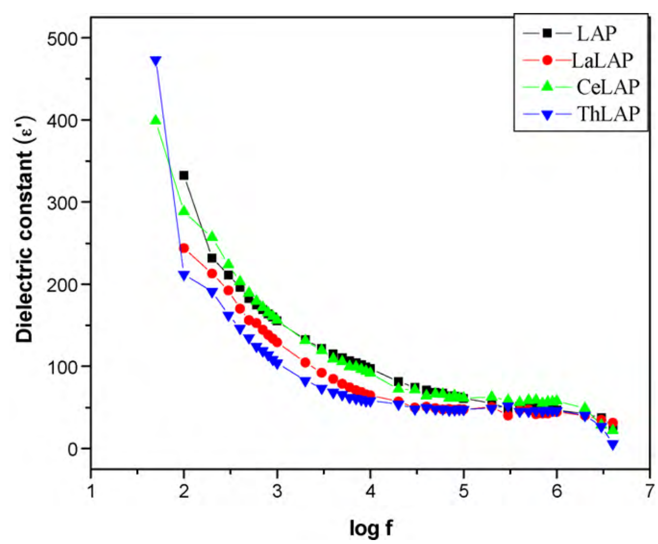

Fig. 4. Dielectric constant versus frequency for LAP, ThLAP, LaLAP and CeLAP single crystals at room temperature.

4.2. Linear and nonlinear optical properties

The optical transmission spectra of pure and rare-earth metal ions doped LAP crystals were recorded in the range 185–1000 nm as shown in Fig. 3. All crystals are transparent in the entire visible region. The transparency in the visible region is a desired property of materials for NLO applications [15,16]. The cut-off wavelengths of ThLAP, LaLAP and CeLAP are found to be 230 nm similar to LAP crystals [17]. It is confirmed from the transmission spectra that the addition of rare-earth metal ions in LAP did not influence the cut-off wavelength. The rare-earth doping in LAP crystal enhances the transmittance of grown crystals.

The powder SHG measurement was carried out for LAP, ThLAP, LaLAP and CeLAP crystals by Kurtz and Perry powder technique [18]. The pulse width of 8 ns from Nd:YAG laser of 1064 nm wavelength was used as input signal for all samples with KDP as the reference. All samples showed green emission confirming the SHG signal. The SHG output voltages of LAP, ThLAP, LaLAP and CeLAP were measured and given in Table 2. The SHG output voltage of the rare-earth metal ions doped LAP crystals increases considerably compared to pure LAP crystal. It has been reported that the SHG efficiency of the crystals can be greatly enhanced by altering the molecular alignment through suitable impurity inclusion [19].

Table 2
SHG output signal of pure and doped LAP crystals.

Sample	SHG output signal (mV)
LAP	661
ThLAP	931
LaLAP	952
CeLAP	681

4.3. Dielectric measurements

Dielectric characteristics are important to study the lattice dynamics of the crystal. It is also useful to understand the nature of defects in the grown crystal [20]. The dielectric studies were carried out for pure and rare-earth metal ions doped LAP crystals in the frequency range from 1 kHz to 7 MHz at room temperature. The dielectric constant ε' was calculated using the relation,

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A}$$

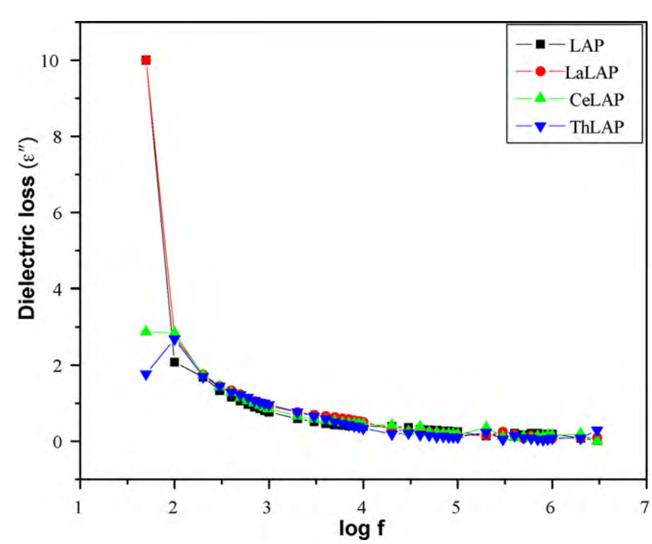

Fig. 5. Dielectric loss versus frequency for LAP, ThLAP, LaLAP and CeLAP single crystals at room temperature.

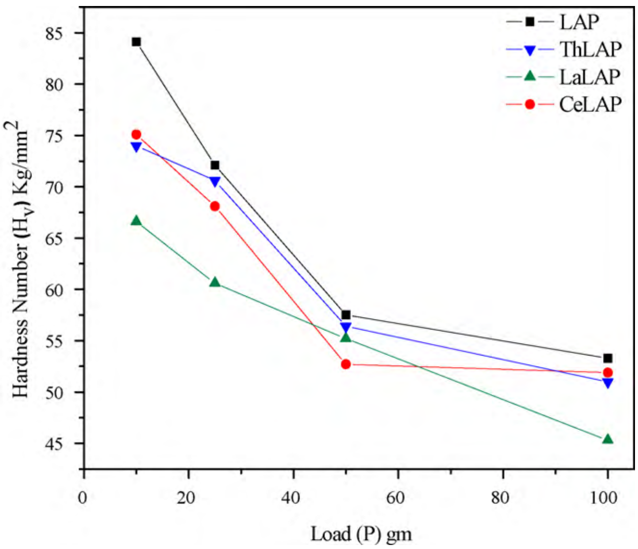

Fig. 6. Microhardness number (H_v) versus Load (P) of pure, Th, La and Ce doped LAP single crystals.

where C is the capacitance, d is the thickness of the crystal, ε_0 is the permittivity of free space and A is the area of the crystal sample. The dielectric loss was calculated using the relation $\varepsilon'' = \varepsilon' D$, where D is the dissipation factor. Figs. 4 and 5 show the dielectric constant ε' and dielectric loss ε'' as a function of frequency at room temperature for LAP, ThLAP, LaLAP and CeLAP crystals. It is observed that the dielectric constant and dielectric loss of pure and rare-earth metal ions doped LAP crystals decreases with increasing frequency and become almost constant at higher frequencies. The high value of dielectric constant at low frequencies may be due to the excitation of bound electrons, lattice vibrations, dipole orientation and space-charge polarization (atomic or electronic) and its low values at higher frequencies may be due to the loss of significance of these polarizations [21]. The dielectric loss of LAP, ThLAP, LaLAP and CeLAP crystals was found to be low at higher frequencies. It reveals that the grown crystals are of good quality with fewer defects [22]. It has been reported that the crystals with high dielectric constant lead to more power dissipation [23]. Since, the dielectric constant value of rare-earth metal ions doped LAP crystals are found to be less than that of LAP crystals, the power dissipation in the doped LAP crystals may be relatively less compared to LAP. Hence, the rare-earth metal ions doped LAP crystals are suitable for electro-optic applications [24].

4.4. Microhardness studies

Hardness of a material is the measure of resistance when it offers to local deformation. The Vicker's hardness number for pure and doped LAP crystals was calculated using,

$$H_v = 1.8544 \left(\frac{P}{d^2}\right) \text{ kg/mm}^2$$

where H_v is the Vicker's hardness number in kg/mm^2, P is the applied load in gm and d is the average diagonal length of the indentation in mm. Crystal samples, free from visible inclusions and cracks, were chosen for microhardness measurements. The indentations were made on the (1 0 0) plane of the crystal samples with applied loads varying from 10 to 100 g with a dwell time of 5 s. The hardness value is taken as the average of the several impressions and the variation of hardness with load is shown in Fig. 6. The hardness is relatively high at lower loads and it decreases for higher loads. Above 50 g load, significant cracking occurred due to the release of internal stress generated locally by the indentation. It is observed that the hardness of pure LAP is higher than that of ThLAP, LaLAP and CeLAP crystals. The change in mechanical strength of the rare-earth doped LAP crystals compared with pure LAP also confirms the incorporation of rare-earth dopants in the LAP crystal lattice.

5. Conclusion

The rare-earth metal ions doping in LAP crystals has induced marginal variations in lattice parameters, peak intensity and cell volume as revealed by X-ray diffraction analysis. The rare-earth dopants in LAP enhanced the transmission percentage of the grown crystals, which suggest the improved optical quality. The powder SHG measurements revealed that the SHG output voltage for the rare-earth doped LAP crystals increases considerably compared to that of LAP. Vicker's hardness number of as-grown crystal of LAP is higher compared to doped LAP crystals. The optical quality and desirable properties of the L-arginine phosphate crystals are significantly enhanced through rare-earth metal ion dopants.

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