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Effect of L-cysteine on optical, thermal and mechanical properties of ADP crystal for NLO application

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ABSTRACT

The ammonium dihydrogen phosphate (ADP) crystal doped with amino acid L-cysteine (LC) was grown by a slow evaporation technique. The grown crystal was transparent in the entire visible region, which is an essential requirement for a nonlinear crystal. The LC doping enhances the optical band gap of ADP (5.35 eV). The TG/DTA analysis of LC doped ADP crystal confirms the optimum thermal stability of grown crystal. The enhancement in the mechanical stability after LC doping was confirmed by Vicker's microhardness test. The LC doping showed significant impact on dielectric properties (dielectric constant and dielectric loss) of grown crystal. The third order nonlinear behavior of LC doped ADP crystal was investigated using a *Z*-scan technique at 632.8 nm and effective nonlinear optical parameters were evaluated.

1. Introduction

The ammonium dihydrogen phosphate (ADP) is an inorganic material widely used as second, third and fourth harmonic generator for Nd: YAG and Nd: YLF lasers. Studies of ADP crystals are gaining more interest because of their unique nonlinear optical, dielectric, piezoelectric and antiferroelectric properties [1–3]. Many researchers have investigated pure and doped ADP crystals to study the enhancement in electrical, nonlinear and ferroelectric properties. The improved optical transmission and electrical conductivity of ADP doped with L-alanine crystals have been reported by Akhtar and Podder [4]. An effect of L-lysine on growth and various properties of ADP has been reported by Rajesh et al. [5]. An effect of L-arginine and glycine on growth and various properties of ADP has been reported by Pattanaboonmee et al. [6]. Structural, optical, dielectric and mechanical study of L-proline doped ADP has been reported by Hasmuddin et al. [7]. Brahim and Bulou [8] have reported growth and detailed analysis of MAS NMR, FT-IR and Raman spectroscopic studies of different mole% LC doped ADP crystal and also reported its tetragonal structure by powder XRD. However, to the best of our knowledge no report is available in the literature on the linear–nonlinear optical, electrical, mechanical and thermal properties of LC doped ADP crystal. Therefore, in the present communication we have reported the effect of LC on linear–nonlinear optical, electrical, mechanical and thermal properties of ADP crystal. These properties are very crucial for any material to be used for NLO applications.

2. Experimental procedure

The amino acid LC was added in three different mole% in the super saturated solution of AR grade ADP. The homogeneous solutions were prepared by constant stirring for 6 h. The solutions were then filtered and kept for slow evaporation at room temperature. The good quality transparent seed crystals were harvested within 7–8 days. The salts of these three mole% LC doped ADP crystals were subjected to SHG test at Indian Institute of Science Bangalore and highest SHG efficiency was observed with 0.08 mole% LC doped ADP crystal powder; hence the bulk crystal of the same was grown by the slow evaporation technique (Fig. 1).

3. Results and discussion

3.1. FT-IR spectral analysis

The FT-IR spectrum of LC doped ADP crystal was recorded using the Bruker α-ATR spectrophotometer in the range of 600–4000 cm^{-1} to confirm the incorporation of LC in ADP crystal. The recorded transmittance FT-IR spectrum of grown crystal is depicted in Fig. 2. In the spectrum the broad band around 3610–2530 cm^{-1} was due to the O–H vibrations of P–O–H group and N–H vibrations of NH_4. The band at 2302 cm^{-1} was observed due to hydrogen bond.

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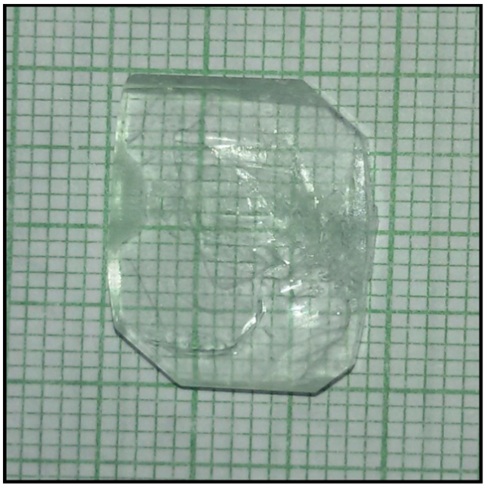

Fig. 1. Photograph of LC doped ADP crystal.

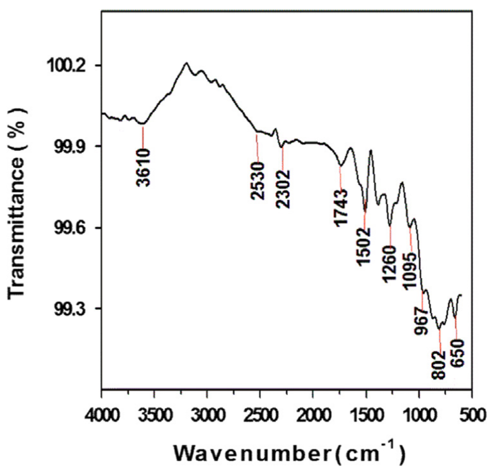

Fig. 2. FT-IR spectrum of LC doped ADP crystal.

The peak at 1502 cm^{-1} was due to N–H vibrations. The strong band at 1260 cm^{-1} was observed due to the combination of the asymmetric stretching vibration of PO_4 with lattice. The peaks at 1095 cm^{-1} and 967 cm^{-1} represent P–O–H vibrations. These peaks are same as those of pure ADP with slight shift in wave numbers from lower to higher, due to the presence of LC in ADP [4,7]. The additional peaks at 1743 cm^{-1} were observed due to C=O stretching and the peak at 650 cm^{-1} was observed due to C–S stretching [8].

3.2. SHG efficiency

The NLO properties of LC doped ADP crystal were studied using a classical Kurtz and Perry powder technique [9] using Q-switched Nd: YAG laser delivering input beam energy of 2.8 mJ/pulse at the wavelength of 1064 nm with repetition rate of 10 Hz and pulse width of 8 ns. The finely powdered samples of 0.08, 0.16, and 0.24 mole% LC doped ADP crystals were tightly packed in the microcapillary tube of uniform bore and illuminated with the polarized beam of laser. The bright green light shown at the output of the subjected samples confirmed the prominent generation of second harmonic signals. The corresponding output voltages recorded for KDP and 0.08 mole% LC doped ADP crystals are 15.2 mV and 31.2 mV. The rise in SHG efficiency of LC doped ADP crystal is observed due to high mobility of charge carriers through π-bonding network of dopant LC. Thus, SHG efficiency of LC doped ADP crystal is nearly double that of KDP suggesting its prominence for NLO application [10].

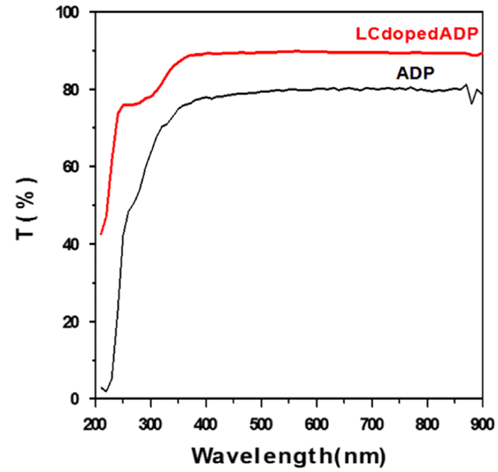

Fig. 3. UV–vis transmittance spectrum.

3.3. UV–visible studies

The UV–visible study of LC doped ADP crystal was undertaken in the range of 200–900 nm using a Shimadzu UV-2450 spectrophotometer. The transmittance spectrum of grown crystal shown in Fig. 3 reveals the large transmission range of doped ADP crystal which is extending to the UV region. This might be due to prominent n to π^* transitions offered by nitrogen and hydrogen bonds in organic compound LC [11]. The transparency of LC doped ADP crystal is more than 89% in entire visible region which confirms its suitability for SHG transmission devices [12]. The dependence of absorption coefficient on incident photon energy helps to evaluate the band gap of material using the relation $(\alpha h\nu)^2 = A(h\nu - E_g)$ [12]. The optical band gap of pure and LC doped ADP crystal was determined using Tauc's extrapolation method as depicted in Fig. 4. The optical band gap of LC doped ADP is found to be 5.35 eV which is greater than pure ADP. The wide optical band gap of LC doped ADP crystal suggests its effective utility for optoelectronic applications [12–14].

3.4. Z-scan studies

The optically transparent LC doped ADP crystal was subjected to *Z*-scan measurement using He–Ne laser operating at 632.8 nm. The polarized Gaussian beam was focused on the crystal through the lens of focal length 12 cm and it was gradually translated along the *Z*-direction pre and post the focus ($Z = 0$). The refraction nonlinearity originated due to localized absorption of repetitive incident optical field was recorded using the closed aperture of an optical detector placed at a far field [15]. The peak to valley transmission difference can be evaluated using following equation [15]:

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta\phi| \tag{1}$$

where $S = [1 - \exp(-2r_a^2/\omega_a^2)]$ is the aperture linear transmittance, r_a is the aperture radius and ω_a is the beam radius at the aperture. The nonlinear refractive index was calculated as

$$n_2 = \frac{\Delta\phi}{KI_0L_{eff}} \tag{2}$$

where $K = 2\pi/\lambda$, I_0 is the intensity of the laser beam at the focus $Z = 0$, $L_{eff} = [1 - \exp(-\alpha L)]/\alpha$ is the effective thickness of the sample depending on linear absorption coefficient (α) and L is thickness of the sample.