Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 136 (2015) 1243–1248

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Study on optical properties of L-valine doped ADP crystal

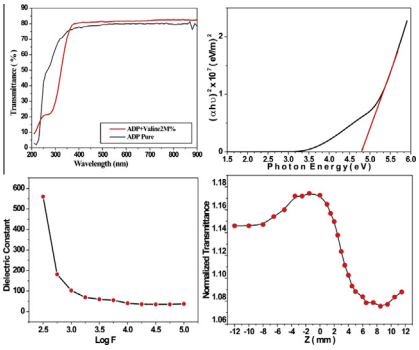
R.N. Shaikh [a], Mohd. Anis [a], M.D. Shirsat [b], S.S. Hussaini [a,*]

[a] Crystal Growth Laboratory, Department of Physics, Milliya Arts, Science and Management Science College, Beed 431122, Maharashtra, India
[b] Intelligent Materials Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431004, Maharashtra, India

HIGHLIGHTS

- Optical and dielectric properties of L-valine doped ADP crystal.
- The SHG efficiency is found to be 1.92 times that of KDP crystal.
- High transparency is useful for optoelectronics applications.
- The lower dielectric characteristics were ascertained from dielectric measurements.
- Third order nonlinearity shows its applications for optical limiting and sensor devices.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 February 2014
Received in revised form 17 August 2014
Accepted 7 October 2014
Available online 20 October 2014

Keywords:
Growth from solution
Nonlinear optical materials
Optical studies
Dielectric studies
Z-scan technique

ABSTRACT

Single crystal of L-valine doped ammonium dihydrogen phosphate has been grown by slow evaporation method at room temperature. The crystalline nature of the grown crystal was confirmed using powder X-ray diffraction technique. The different functional groups of the grown crystal were identified using Fourier transform infrared analysis. The UV–visible studies were employed to examine the high optical transparency and influential optical constants for tailoring materials suitability for optoelectronics applications. The cutoff wavelength of the title crystal was found to be 280 nm with wide optical band gap of 4.7 eV. The dielectric measurements were carried to determine the dielectric constant and dielectric loss at room temperature. The grown crystal has been characterized by thermogravimetric analysis. The second harmonic generation efficiency of the grown crystal was determined by the classical Kurtz powder technique and it is found to be 1.92 times that of potassium dihydrogen phosphate. The grown crystal was identified as third order nonlinear optical material employing *Z*-scan technique using He–Ne laser operating at 632.8 nm.

Introduction

Ammonium dihydrogen phosphate (ADP) crystal is an interesting inorganic material with allied non linear optical (NLO), dielectric and antiferroelectric properties with a wide scope of distinct applications such as electro optic modulator, parametric generators, optical switches in inertial confinement fusion and acoustic–optical devices. The amino acids contains a deprotonated carboxylic group (COOH) and protonated amino group (NH_2), which makes them ideal candidates for NLO applications. The effect of amino acids on the growth and properties of different material crystals have been reported for NLO applications [1–6]. According to literature survey, improved physico-chemical properties of ADP has been achieved by adding DL-malic acid and the effect of amino acids viz. Glycine, L-alanine, L-lysine on structural, thermal, optical and electrical properties have been reported [7–10]. Josephine et al. reported the studies on structural and

* Corresponding author. Mobile: +91 9325710500.
E-mail address: shuakionline@yahoo.co.in (S.S. Hussaini).

http://dx.doi.org/10.1016/j.saa.2014.10.009
1386-1425/

optical transmission spectra of valine added ADP crystal [11]. To the best of our knowledge no systematic data on optical constants, optical band gap, dielectric studies, SHG efficiency, thermal behavior and third order nonlinear properties of L-valine doped ADP have been reported. Thus present investigation is first of its kind to report studies on L-valine doped ADP crystal characterized by dielectric studies, SHG efficiency test, thermogravimetric analysis, *Z*-scan measurements, along with detailed evaluation of linear optical constants.

Experimental procedure

Crystal growth

The AR grade ADP salt was gradually dissolved in deionized water until a saturated solution was obtained. In the saturated solution of ADP prepared in separate beakers, the calculated amount of 1 and 2 mol% L-valine was added with constant stirring. The prepared solutions were allowed to evaporate at room temperature to procure the respective salts. The purity of the doped compounds was gained by successive recrystallisation using deionized water. The Kurtz–Perry powder test revealed that the SHG efficiency was found to be enhanced with 2 mol% L-valine in ADP crystal. Hence, the saturated solution of 2 mol% L-valine doped ADP was prepared and allowed to evaporate at room temperature. The well phased, good quality transparent seeds were harvested within 8–10 days. The photograph of 2 mol% L-valine doped ADP crystal of dimension $12 \times 14 \times 3\ mm^3$ is shown in Fig. 1.

Results and discussion

NLO studies

The Kurtz and Perry powder test was performed to determine the effective second harmonic generation efficiency of the grown crystal. The 1 and 2 mol% L-valine doped ADP samples were finely powdered and subjected to SHG test. The crystalline powder was illuminated by Nd:YAG laser operating at 1064 nm having input beam energy of 2.8 mJ/pulse, pulse width of 8 ns and repetition rate of 10 Hz. The second harmonic signals generated in the crystalline samples were confirmed from emission of green radiation. The SHG efficiency of 2 mol% L-valine doped ADP crystal was found to be 1.92 times that of potassium dihydrogen phosphate (KDP). Thus grown crystal may be efficient NLO material for applications in second harmonic generation and electro-optic devices [12].

Powder X-ray diffraction (XRD) analysis

The grown crystal was characterized by powder XRD technique to confirm the crystallinity. The indexed XRD pattern of grown crystal in the range of $10–50^{\theta}$ is shown in Fig. 2. The evaluated cell parameters of the grown crystal are $a = b = 7.497$ Å and $c = 7.534$ Å $\alpha = \beta = \gamma = 90^{\circ}$ which are in good agreement with the reported work [11]. The obtained peaks and evaluated lattice parameters revealed that the addition of L-valine did not change the tetragonal structure of ADP.

FT-IR analysis

The FT-IR transmission spectra of L-valine doped ADP crystal was recorded using Bruker α-ATR instrument in the range 600–4000 cm^{-1}. The spectrum of doped ADP crystal is shown in Fig. 3. The characteristic peaks of functional groups of ADP are observed at 3257, 1641, 1409, 1288, 1097, 907 [11]. The band observed at 3229 cm^{-1} includes O–H vibrations and N–H vibration of amino acid and the P–O–H vibrations at 1097 and 907 cm^{-1} of the pure ADP are shifted to 1062.86 and 908.92 cm^{-1}, which may be due to the incorporation of L-valine in ADP crystal.

Optical studies

Optical studies for grown solid crystal were carried using Shimadzu UV-2450 spectrophotometer in the range 200–900 nm. The UV cut off wavelength of grown crystal was revealed to be 280 nm ascertained from recorded transmission spectra cited in Fig. 4(a). The high transparency in visible region and lower cutoff wavelength of the grown crystal suggests its suitability for applications in UV tunable lasers [13]. The measured transmittance data was used to calculate absorption coefficient (α) from the relation.

$$\alpha = (1/t)\ln(1/T) \quad (1)$$

where T is the transmittance and t is the thickness of the crystal.

Optical band gap was evaluated from the absorption spectrum and optical absorption coefficient (α) near the absorption edge is given by:

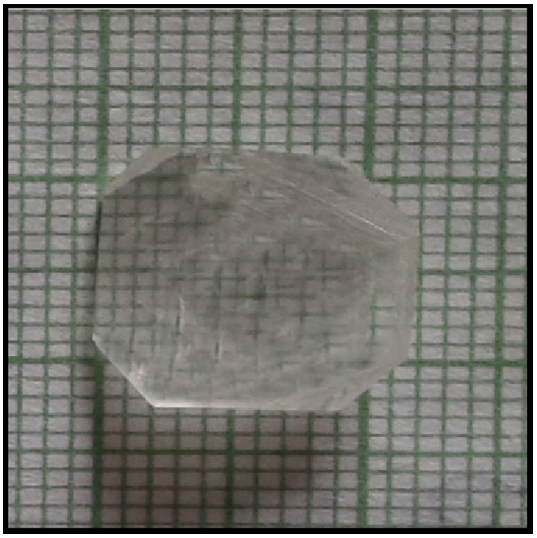


Fig. 1. Photograph of doped ADP crystal.

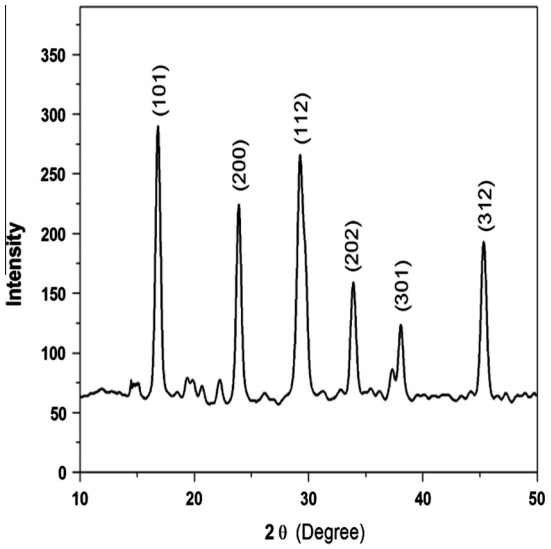


Fig. 2. Powder XRD pattern of as grown crystal.

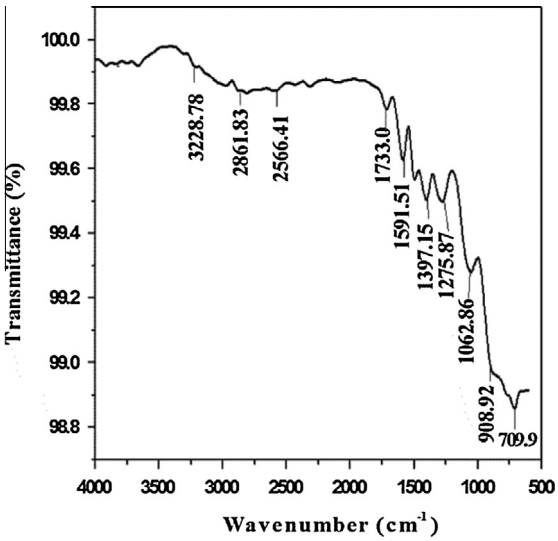


Fig. 3. FTIR spectrum of doped ADP crystal.

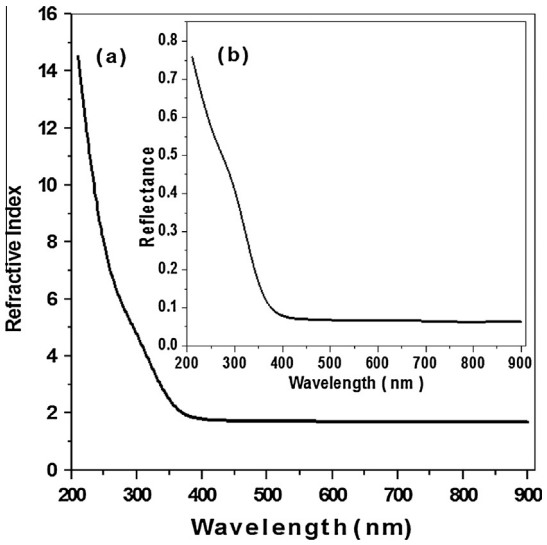


Fig. 5. (a) Refractive index vs. wavelength. (b) Reflectance vs. wavelength.

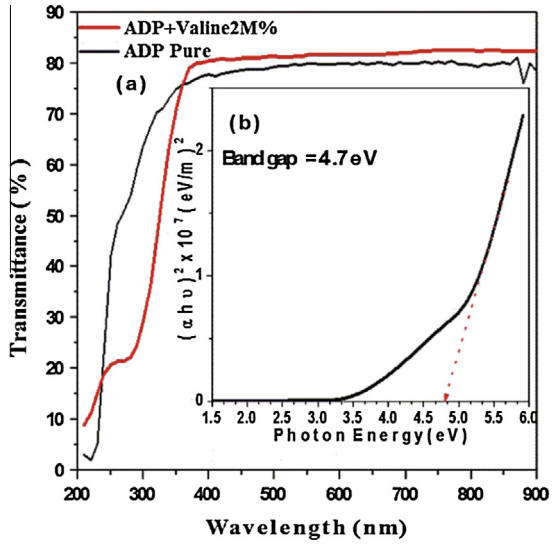


Fig. 4. (a) UV–visible spectrum. (b) $(\alpha hv)^2$ vs. photon energy (hv).

$$\alpha hv = A\sqrt{hv - E_g} \tag{2}$$

where E_g is the optical band gap of the crystal and A is a constant.

The optical band gap of doped ADP crystal was calculated from the Tauck's extrapolation plot depicted in Fig. 4(b). It is found to be 4.7 eV which is desirable quality for applications in optoelectronics devices [14]. The propagation of light through material medium can be tailored by evaluating the refractive index of the grown crystal. The profile of refractive index, $n = (1/T + (1/T - 1))$ and reflectance, $R = ((n-1)^2/(n+1)^2)$ of the grown crystal are depicted in Fig. 5(a and b) respectively [15,16]. The high transmission, lower reflectance and refractive index in entire visible region indicate the potential candidature of grown crystal for antireflection coating in solar thermal devices [5,17]. The high photonic response of optical conductivity ($\sigma = \alpha nC/4\pi$) for the grown crystal can be ascertained from the graph depicted in Fig. 6. The optical conductivity increases with increase in photon energy which is desirable property for information processing and computing [18]. The plot of complex dielectric constant ($\varepsilon_c = \varepsilon_r + \varepsilon_i$) is shown in Fig. 7. The lower dielectric constant and the higher optical response suggest the better conversion efficiency of the material [18]. The potential optical properties of the grown crystal suggest its suitability for distinct integrated optical applications.

Thermogravimetric analysis

The thermogravimetric analysis (TGA) of grown crystal was carried using the TQA-500 thermogravimetric analyzer in a nitrogen atmosphere at heating rate of 25 °C/min. The TGA trace of grown crystal is shown in Fig. 8. The bulk weight loss of the sample is observed at 190 °C which indicates the decomposition of volatile components of the material. Thus the grown crystal is resistant to thermal exposure up to 190 °C which is comparable but slightly lower than pure ADP [10].

Dielectric studies

The grown crystal was subjected to dielectric studies using the Multi frequency LCR meter (LCR-819 series, Gwinstek Instrument). The dielectric analysis is an essential characteristic of material that

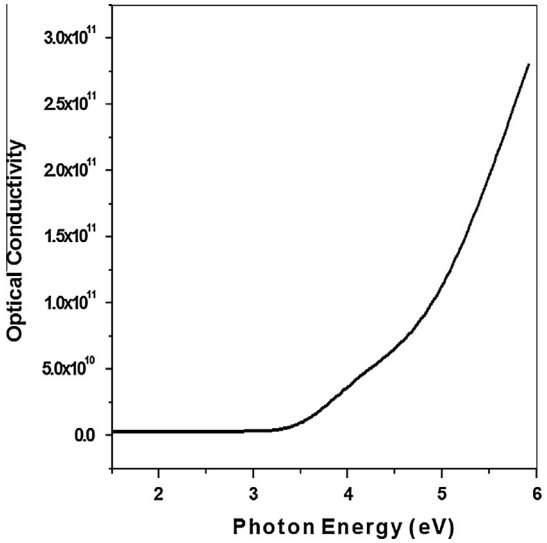


Fig. 6. Optical conductivity vs. photon energy.

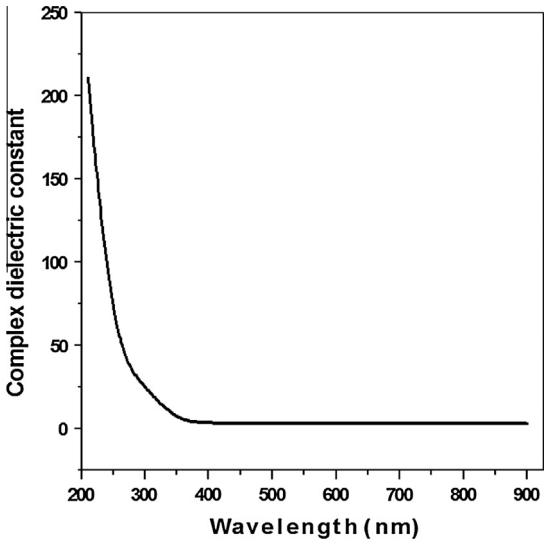


Fig. 7. Complex dielectric constant vs. wavelength.

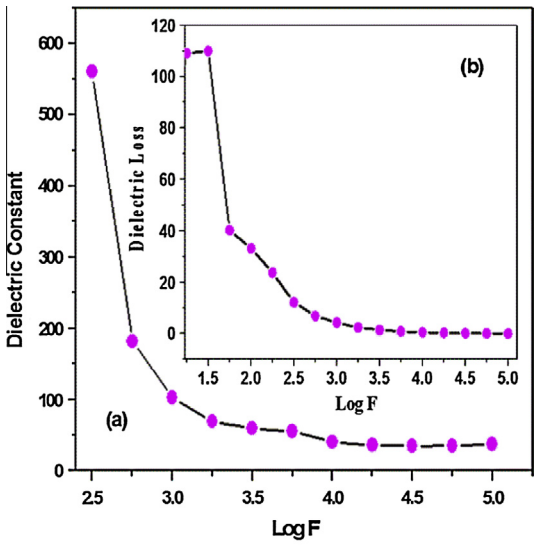


Fig. 9. (a) Dielectric constant vs. Log*F*. (b) Dielectric loss vs. Log*F*.

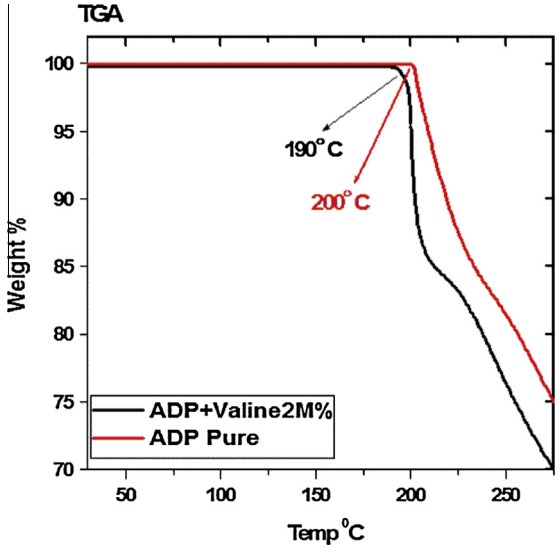


Fig. 8. TGA curve of grown crystal.

can be used to fetch information based on the electrical properties of a material medium as a function of frequency. Dielectric properties are imperative to meet the objectives of electro-optic properties of the crystal specifically for non conducting materials [19]. The dielectric constant and dielectric loss have been calculated using the formula,

$$\varepsilon = cd/\varepsilon_0 A \tag{3}$$

$$\text{Dielectric loss} = \text{Tan}\,\delta = \varepsilon/\varepsilon_0 \tag{4}$$

where c is the capacitance, d is the thickness of the sample, A is the area of the sample.

Fig. 9 represents the frequency dependent variation of dielectric constant and dielectric loss at room temperature. The values of dielectric constant and dielectric loss decreases with the increasing frequency, this may be due to subsequently decreasing contribution of all the four polarizations viz. electronic, ionic, orientation, and space charge, which are predominant in the lower frequency region [20]. The decreased dielectric constant and dielectric loss at higher frequencies indicates that the sample possesses enhanced optical quality with lower defects and this parameter is of vital importance for NLO applications [14,21].

Z-scan studies

The single-beam *Z*-scan is an effective technique to determine the third order nonlinear optical properties of the materials. The simultaneous measurement can be carried using open and closed aperture data to examine the nature of nonlinear index of refraction (n_2) and nonlinear absorption coefficient (β). The study of nonlinear refraction phenomenon can be analyzed using the closed aperture *Z*-scan technique. The Gaussian beam was focused on the crystal using a lens of focal length 12 cm and the crystal was then translated along the Z direction. The phenomenon of change in transmitted intensity about the focus ($Z = 0$) i.e. change in nonlinear refraction occurring due to higher repetitive rate of laser beam was monitored through the closed aperture of optical detector placed at a far field [22]. The details of *Z*-scan setup are given in Table 1. The difference between the peak and valley transmission (ΔT_{p-v}) is written in terms of the on axis phase shift at the focus as [23],

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta\phi| \tag{5}$$

where S is the aperture linear transmittance and is calculated using the relation

$$S = 1 - \exp(-2r_a^2/\omega_a^2) \tag{6}$$

where r_a is the aperture and ω_a is the beam radius at the aperture. The nonlinear refractive index is given by:

Table 1
Optical detail of *Z*-scan setup and measured parameters.

Laser beam wavelength (λ)	632.8 nm
Lens focal length (f)	12 cm
Optical path distance (Z)	115 cm
Spot-size diameter in front of the aperture (ω_a)	1 cm
Aperture radius (r_a)	4 mm
Incident intensity at the focus ($Z = 0$)	3.13 MW/cm^2
Sample thickness	2 mm
Effective thickness (L_{eff})	1.81 mm
Nonlinear refractive index (n_2)	-4.5×10^{-12} cm^2/W
Nonlinear absorption coefficient (β)	5.79×10^{-6} cm/W
Third-order nonlinear susceptibility (χ^3)	2.249×10^{-5} esu

$$n_2 = \frac{\Delta\phi}{KI_0L_{eff}} \tag{7}$$

where $K = 2\pi/\lambda$ (λ is the laser wavelength), 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, α is the linear absorption and L is the thickness of the sample. From the open aperture Z-scan data, the nonlinear absorption coefficient is estimated as:

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0L_{eff}} \tag{8}$$

where ΔT is the one valley value at the open aperture Z-scan curve. The value of β will be negative for saturable absorption and positive for reverse saturable absorption (RSA). The expressed RSA observed in the crystal is viewed as a consequence of two-step (excited state) absorptions of optical energy for which the nonlinearity can be considered as an "effective" two-photon absorption process [24]. The real and imaginary parts of the third order nonlinear optical susceptibility $\chi^{(3)}$ are defined as,

$$\mathrm{Re}\,\chi^{(3)}\ (\mathrm{esu}) = 10^{-4}(\varepsilon_0 C^2 n_0^2 n_2)/\pi\,(\mathrm{cm}^2/\mathrm{W}) \tag{9}$$

$$\mathrm{Im}\,\chi^{(3)}\ (\mathrm{esu}) = 10^{-2}(\varepsilon_0 C^2 n_0^2 \lambda\beta)/4\pi^2\,(\mathrm{cm}/\mathrm{W}) \tag{10}$$

where ε_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample and c is the velocity of light in vacuum. Thus, we can easily obtain the absolute value of χ^3 using equation,

$$\chi^3 = \sqrt{(\mathrm{Re}\,\chi^3)^2 + (\mathrm{Im}\,\chi^3)^2}\ \mathrm{esu} \tag{11}$$

The closed aperture transmittance data depicted in Fig. 10 confirms the self defocusing nature as prefocal transmittance peak is followed by the postfocal transmittance valley, indicating negative index of refraction.

The negative index of refraction of doped ADP crystal suggests its prominence for protection of optical night vision sensor devices [25]. The nonlinear refractive index is found to be -4.5×10^{-12} cm^2/W. The open aperture transmittance data of grown crystal confirmed the effective RSA depicted in Fig. 10. The open aperture transmittance data was employed to evaluate the nonlinear absorption coefficient (β) of the grown crystal. The effective β value of doped ADP crystal is found to be 5.79×10^{-6} cm/W which is relatively lower than potential NLO material [26]. The nonlinear third order susceptibility of doped ADP crystal is found to be 2.249×10^{-5} esu which is notably greater than efficient third order NLO crystals [5,27]. The higher susceptibility originates as a result of enhanced delocalization of π-electron cloud resulting to high polar nature [28]. The promising third order NLO properties of doped ADP crystals suggest its suitability for applications in optical limiting and sensor devices [29].

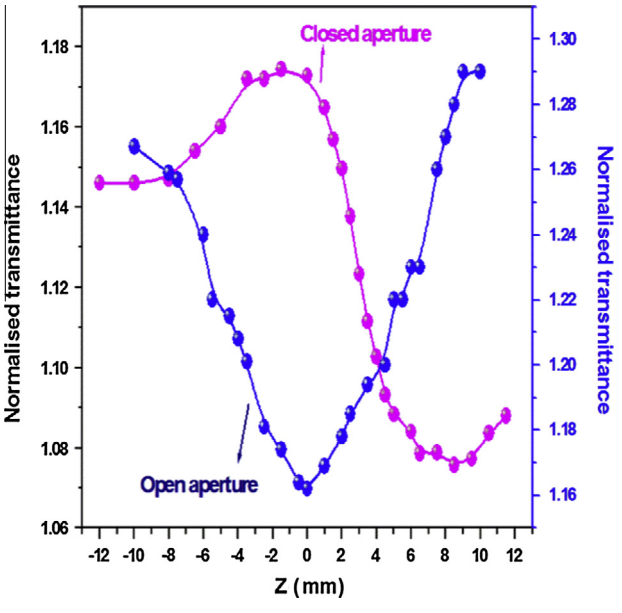


Fig. 10. Closed and open aperture Z-scan curve.

Conclusion

The two mol% L-valine doped ADP crystal has been grown by slow evaporation method at room temperature. The lattice parameters of grown crystal were confirmed through powder XRD technique. The optical studies confirmed the high transparency and encouraging optical constants in the entire visible region. The wide band gap of doped ADP crystal was found to be 4.7 eV, suitable for optoelectronics applications. The Thermal studies revealed that the grown crystal may be subjected to NLO applications up to 190 °C. The lower dielectric constant and dielectric loss at higher frequencies were examined by dielectric studies. The SHG efficiency of grown crystal was determined to be 1.92 times that of KDP. The grown crystal showed potential third order nonlinear optical parameters ascertained from Z-scan technique at 632.8 nm. All above studies suggests the prominence of grown crystal for laser stabilization, microelectronics and integrated optical applications.

Acknowledgments

The authors are thankful to the Department of Science and Technology, India, and University Grants Commission, New Delhi, India, for financial assistance. The authors are also thankful to Prof. D. Sastikumar, Department of Physics, National Institute of Technology, Tiruchy, India for extending the facility for Z-scan measurement.

References

[1] P. Rajesh, P. Ramasamy, Spectrochim. Acta A 74 (2009) 210–213.
[2] P. Rajesh, P. Ramasamy, Mater. Lett. 63 (2009) 2260–2262.
[3] M.D. Shirsat, S.S. Hussaini, N.R. Dhumane, V.G. Dongre, Cryst. Res. Technol. 43 (2008) 756–761.
[4] N.R. Dhumane, S.S. Hussaini, V.G. Dongre, P.P. Karmuse, M.D. Shirsat, J. Cryst. Res. Technol. 44 (2009) 269–274.
[5] R.N. Shaikh, Mohd Anis, M.D. Shirsat, S.S. Hussaini, IOSR J. Appl. Phys. 6 (2014) 42–46.
[6] P. Rajesh, P. Ramasamy, G. Bhagavannarayana, J. Cryst. Growth 311 (2009) 4069–4075.
[7] P. Rajesh, P. Ramasamy, J. Cryst. Growth 311 (2009) 3491–3497.
[8] Ferdousi Akhtar, Jiban Podder, J. Cryst. Process. Technol. 1 (2011) 18–25.
[9] N. Pattanaboonmee, P. Ramaswamy, R. Yimnirun, P. Manyum, J. Cryst. Growth 314 (2011) 196–201.
[10] P. Rajesh, P. Ramasamy, C.K. Mahadevan, J. Cryst. Growth 311 (2009) 1156–1160.
[11] T. Josephine Rani, Fernando Loretta, S. Ramalingom, S. Perumal, Optics: Phenomena, Opt.: Phenom. Mater. Dev. Charact. AIP Conf. Proc. 1391 (2011) 146–148, http://dx.doi.org/10.1063/1.3646806.
[12] L.P. Nair, B.R. Bijini, S. Prasanna, C.M.K. Nair, M. Deepa, K. Rajendra Babu, Spectrochim. Acta A 120 (2014) 517–523.
[13] P. Vivek, P. Murugakoothan, Opt. Laser Technol. 49 (2013) 288–295.
[14] D. Kalaiselvi, R. Jayavel, Appl. Phys. A 107 (2012) 93–100.
[15] N.A. Bakr, A.M. Funde, V.S. Waman, M.M. Kamble, R.R. Hawaldar, D.P. Amalnerkar, S.W. Gosavi, S.R. Jadkar, J. Phys. 76 (2011) 519–531.
[16] R. Robert, C. Justin Raj, S. Krishnan, R. Uthrakumar, S. Dinakaran, S. Jerome Das, Physica B 405 (2010) 3248–3252.
[17] R. Santhakumaria, K. Ramamurthy, Spectrochim. Acta A 78 (2011) 653–659.
[18] T.C. Sabari Girisun, S. Dhanuskodi, Cryst. Res. Technol. 44 (2009) 1297–1302.
[19] S. Boomadevi, H.P. Mittal, R. Dhansekaran, J. Cryst. Growth 261 (2004) 55–62.
[20] M. Meena, C.K. Mahadevan, Cryst. Res. Technol. 43 (2008) 166–172.
[21] S. Suresh, A. Ramanand, D. Jayaraman, P. Mani, J. Optoelectron. Adv. Mater. 4 (2010) 1763–1765.

[22] S. Dhanuskodi, A. Philominal, J. Philip, K. Kim, J. Yi, J. Mater. Sci. 46 (2011) 3169–3175.
[23] Mohd. Anis, M.D. Shirsat, G. Muley, S.S. Hussaini, Physica B 449 (2014) 61–66.
[24] D. Sajan, N. Vijayan, K. Safakath, R. Philip, I. Hubert Joe, J. Phys. Chem. A 115 (2011) 8216–8226.
[25] P.V. Dhanaraj, N.P. Rajesh, J. Cryst. Growth 318 (2011) 974–978.
[26] G. Pabitha, R. Dhanasekaran, Opt. Laser Technol. 50 (2013) 150–154.
[27] P.T. Anusha, P. Silviya Reeta, L. Giribabu, S.P. Tewari, S. Venugopal Rao, Mater. Lett. 64 (2010) 1915–1917.
[28] P. Srinivasan, A.Y. Nooraldeen, T. Kanagasekaran, A.N. Dhinaa, P.K. Palanisamy, R. Gopalakrishnan, Laser Phys. 18 (2008) 790–793.
[29] T. Kanagasekaran, P. Mythili, P. Srinivasan, A.Y. Nooraldeen, P.K. Palanisamy, R. Gopalakrishnan, Cryst. Growth Des. 8 (2008) 2335–2339.