Growth and properties of ADP single crystal

Shaikh Kalim¹, A. B. Lad¹ and B. H. Pawar²

¹Amolakchand Mahavidyalaya, Yavatmal, Maharashtra, India
²Department of Physics, Sant Gadge Baba, Amravati University, Amravati, Maharashtra, India

ABSTRACT

Ammonium dihydrogen phosphate (ADP) is an excellent inorganic nonlinear optical material with different device applications. In the present work, single crystal of pure ADP crystal has been grown from the aqueous solution by slow evaporation technique. The grown crystals have been subjected to various characterizations studies like UV-visible, FTIR spectroscopy and dielectric studies. FTIR spectrum analysis confirmed the presence of functional groups of ADP crystal. UV-visible studies suggest that the crystal is suitable for nonlinear applications. Dielectric studies confirmed the single phase and high purity of the crystal. During the growth it has been observed that the low evaporation rate gives good quality crystals.

Key words: UV-Visible spectra, transparency, SHG efficiency and FT-IR spectra etc.

INTRODUCTION

ADP is widely used as the second, third and fourth harmonic generator of Nd: YAG and Nd: YLF lasers. The crystal is widely used for electro-optical applications such as Q-switch for Nd: YAG, Nd: YLF and Ti-sapphire lasers as well as for acoustic-optical applications [1-3]. Single crystals of ADP are used for frequency doubling and tripling of laser system [1].ADP has gained considerable importance in recent years because of its nonlinear, ferroelectric, piezoelectric and electro-optical properties. We have made an attempt to modify ADP crystal by controlling crystal growth parameter like temperature and growth rate etc. A simple localized- bond charge model for the calculation of nonlinear optical susceptibility is presented as per it there are three important contribution to nonlinearity namely the bond ionicity, the difference in atomic radii of the bonded atoms and d-electrons contributions [4], e.g. ZnS, ZnO BeO, CuCl, AlPO₄, NH₄PO₄ and KH₂PO₄ these crystals are highly anisotropic. Higher efficiency of frequency conversion can be achieved by growing good quality crystal and increasing the intensity of the input signal.

The ideal material that could have potential applications nonlinear optical devices should possess the combination of large nonlinear figure of merit for frequency conversion, high laser damage threshold, fast response time and wide phase match able angle, architecture flexibility for molecular designed and morphology, optical transparency and high mechanical strength [8-12]. Pure ADP crystal grown may fulfil many of these requirements but there are some drawbacks such as environmental stability, poor chemical stability and poor phase match angle.

In unsaturated solution, anionic groups exist as free hydrated ions, in saturated solution the H₂PO₄⁻ groups are interconnected via H-bonds. The change in NH₄⁺ configuration is subject to external asymmetric attractions induced the presence of H₂PO₄⁻ dimmer with increase of concentration. In ADP growth process, configuration of anions group undergoes a continuously adjusting process with prolonging the growth time, the tapered ADP crystallites occur and tapering becomes more intense with decrease of supersaturating arising from competitive growth of NH₄⁺ and K⁺ ions. Hence slow evaporation rate can give better quality crystals with high value of damage threshold value. Crystallization behaviour of inorganic material strongly depends on chemical bonding characteristics during the growth processes, which builds a bridge between thermodynamics and kinetic controls. Specific growth morphology controls can be realized by chemical tuning and detailed dynamic bonding environments of surface atoms [13].
Laser damage threshold and energy band gap is related for the NLO crystal. It is found that if the normalized LDT of NLO crystal is required to be higher than 1 (corresponding to about 100MW/cm² for nanosecond laser, which is enough for all academic and commercial purposes) the energy band gap should be larger than 3 eV [5]. The grown crystals have band gap more than 3 eV.

**MATERIALS AND METHODS**

A Single crystal of pure ADP was grown from the saturated solution at 32 °C by slow evaporation method using AR grade samples of ADP. Solution is stirred for one hour using magnetic stirrer and filtered using Whitman filter paper. The filtered solution was transferred to borosil glass beaker; it was kept opened and was kept in a constant temperature bath at 32°C in a dust free atmosphere. After fifteen days good quality single crystals were obtained. All the crystals were colourless, stable and transparent. The crystal was characterized using FTIR, UV-visible spectroscopy and dielectric constant is determined using LCR meter in a range 100HZ to 10khz.

**RESULT AND DISCUSSION**

**UV-visible spectroscopy**

This shows that lower cut of frequency is 200nm this crystal is transparent between 220nm to 800nm, so is a good nonlinear crystal

The single crystal of ADP is mainly used for optical applications. The study of the optical transmission range of the grown crystal is thus very important. UV-visible transmission spectra were recorded using Shimatzu UV-Visible Spectrometer in the range 200nm -800nm. ADP crystal showed good transmittance in the entire UV-visible region.

**FTIR Spectroscopy study:**

In the spectrum of pure ADP crystal the broad band around 3250 cm⁻¹ was due to the O-H vibrations of water, P-O-H group and N-H vibrations of ammonium. The band at 2387 cm⁻¹ was assigned to hydrogen bond. The broadness was due to the hydrogen bonding interaction with adjacent molecules. The O-H bending vibrations gave the peaks at
1706, 1642 cm$^{-1}$. The peak at 1409 cm$^{-1}$ was due to the bending vibrations of ammonium. The medium bands at 560, 405 are due to PO$_4$ vibrations.

**Powder SHG measurement**

The SHG intensity of the samples were tested by the modified version of the powder technique developed by Kurtz and Perry in 1968 using Quanta Ray Spectra Physics model: Prolab 170 Nd: YAG 10ns laser with a pulse repetition rate of 10HZ working at 1064nm at the department of Inorganic Physical Chemistry, Indian Institute of Science Bangalore. The energy per pulse is 4.4mj. The SHG was confirmed by the emission green radiation ($\lambda$ = 532nm) which was finally detected by a photomultiplier tube and displayed on the oscilloscope. Measured powder SHG efficiency of pure ADP is 123mV and for KDP 71mV.

**Dielectric study**

The capacitance was measured using convectional parallel plate capacitor method with frequency range (100Hz to 10 KHz) using Falcon LCR-010B LCR meter. The dielectric properties are correlated with the electro-optic properties of the crystals. The magnitude of dielectric constant depends on the degree of polarization charge displacement of the crystals. The dielectric constant of materials is due to the contribution of electronic, ionic and dipolar and space charge polarization which depend on the frequency [6]. At lower frequency all the polarizations are active. The space charge polarization is generally active at low frequency and at high temperature [7].

In KDP and ADP crystals many reports are available about its behaviour and in our present work the measured dielectric constant values are in good agreement with the reported results. Value of dielectric constant decreases with increase in frequency and lower value of dielectric constant may suggest the purity of the crystal and high damage threshold of the crystal.

**CONCLUSION**

Transparent, colourless crystals of pure ADP single crystals were grown by slow evaporation technique at 32$^\circ$C. FTIR study confirms the presence of functional groups in crystals. The absorption spectra reveals that grown crystals have better optical transparency and have sufficient transmission in UV-visible and IR regions. The lower cut-off wavelength is found to be 200nm. It has been observed that enhanced transparency is better for good NLO efficiency. Dielectric constant study reveals that the dielectric constant goes on decreasing on increasing frequency suggest the purity of crystal and hence improved damage threshold value of crystal.

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