Optical Materials 42 (2015) 87–93

Contents lists available at ScienceDirect

Optical Materials

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

Growth and characterization of large size ADP single crystals and the effect of glycine on their growth and properties

P. Rajesh *, P. Ramasamy

Centre for Crystal Growth, SSN College of Engineering, Kalavakkam 603 110, India

A R T I C L E I N F O

Article history:
Received 15 October 2014
Received in revised form 15 December 2014
Accepted 17 December 2014
Available online 19 January 2015

Keywords:
X-ray diffraction
Growth from solutions
Single crystal growth
Optical materials

A B S T R A C T

$80 \times 50 \times 50$ mm^3 size 1 mol% of glycine added ADP single crystals have been grown by ACRT technique. The grown crystals have been subjected to powder XRD, FTIR, UV–Vis, HRXRD, TG/DTA, microhardness, laser damage threshold, piezoelectric, dielectric and SHG studies. The crystallinity and the functional groups are confirmed by powder XRD and FTIR spectroscopy. Good transparency in the entire visible region which is an essential requirement for a nonlinear optical crystal is observed for the grown crystals. The structural perfection of the grown crystal has been analyzed by high resolution X-ray diffraction rocking curve measurements. Compared to pure ADP crystal higher hardness was observed from the Vickers hardness studies. Shift in the decomposition temperature has been observed from TG/DTA. Dielectric constant and dielectric loss were measured for the grown crystals for different frequencies and temperatures. Significant piezoelectric charge coefficient has been noted for the glycine doped crystals. Laser damage threshold value has been determined using Nd:YAG laser. Powder SHG measurements show the suitability of the ingot for nonlinear optical applications.

1. Introduction

Nonlinear optical crystals with high conversion efficiencies of the second, third and fourth harmonics generation, transparent within a broad spectral range are required for numerous applications. In particular KDP and ADP crystals are widely used for frequency conversion and optical switching in modern optoelectronics and photonics. Moreover, these crystals are successfully used as a model system for studying the mechanism of crystal growth from the solution, as well as for finding out a relation between NLO properties and the crystal structure. Unremitting interest to KDP type crystals is caused by their unique physical properties and high manufacturability. In particular, ADP and KDP crystals which possess extremely high optical and structural perfection make it possible to produce elements for doubling and tripling of laser radiation frequency, electro-optic switches and modulators with an aperture of several tens and hundreds of square centimeters to be used, e.g. in laser fusion facilities [1–6]. Zaitseva et al. of LLNL grew large-scale (40–55 cm) KDP crystals at rates of 10–20 mm/d, the rapid growth method is based on the use of “point seed” [7].

In the field of nonlinear optical crystal growth, amino acids are playing a vital role. Many numbers of natural amino acids are individually exhibiting the nonlinear optical effect. Complex of amino acids are promising material for optical second harmonic generation. The demand for large-size ADP and KDP-type single crystals has increased sharply in recent years because these crystals have important piezoelectric, ferroelectric, electro-optic and nonlinear optical properties [8–10]. Such demand requires the rapid growth of crystals in a shorter duration of time while maintaining the quality and size. In parallel to the invention of new NLO materials, it is also important to modify the physical, optical, and electrical properties of these materials either by adding functional groups or incorporation of dopants for tailor made applications. In the presence of dopants growth promoting factors like growth rate and many of the useful physical properties like optical transparency, second harmonic generation (SHG) efficiency, laser damage threshold (LDT), etc., get enhanced. The dopants or additives also influence the crystalline perfection which may in turn influence the physical properties depending on the degree of doping and as per the accommodating capability of the host crystal. Keeping this in our mind, in our laboratory it was proposed to grow ADP crystal added with 1 mol% of glycine. Glycine, the simplest aminoacid, has three polymeric crystalline forms: α, β and γ. Both α and β forms crystallize in centrosymmetric space group P21/c. γ-glycine crystallizes in non-centrosymmetric space group P31 making it a candidate for piezo-electric and NLO applications [11].

In this work, we have presented the growth, structural, optical, thermal, mechanical, dielectric and SHG efficiency of glycine doped

* Corresponding author. Tel.: +91 9840522490; fax: +91 44 27475166.
E-mail addresses: rajeshp@ssn.edu.in, rajeshppraj@gmail.com (P. Rajesh).

http://dx.doi.org/10.1016/j.optmat.2014.12.024
0925-3467/© 2014 Elsevier B.V. All rights reserved.

ADP single crystals grown by slow cooling method. The effects of impurity atoms on the quality and performance of the crystals are analyzed. The results of the doped ADP crystals are compared with the results of the pure ADP crystals.

2. Experimental procedure

2.1. Solubility

ADP is purified by several times of recrystallization in deionized water. The resistivity of the used deionized water is 18 MΩ-cm. The solubility of pure ADP in deionized water was reported by us [12]. In order to know the effect of glycine in solubility of ADP, the 1 mol% of glycine is dissolved fully in 100 ml deionized water and the solubility of ADP is gravimetrically analyzed using the solution. Comparing the result with the pure ADP it is found that the addition of glycine has decreased the solubility of the pure ADP. Similar results have been reported by us in ammonium acetate added ADP [12]. The solubility curve is shown in Fig. 1.

2.2. Crystal growth

The crystal growth has been carried out using slow cooling method. The starting material was ADP pure reagents (G.R., Merck). Pure water by Milli-Q ultrapure water purification system with resistivity of 18.2 MΩ-cm was used as the solvent. Glycine (G.R., Merck) was used as dopant. All experiments are carried out in a standard glass 5000 ml crystallizer, used for conventional crystal growth by the method of temperature reduction. The temperature of crystallizer is controlled using an external water bath, and the temperature fluctuations are less than ±0.01 °C. The reversible rotation rate of the platform with the crystal was about 35 rpm. The solutions with 1 mol% glycine are filtered through filters with a pore diameter of 0.15 μm to remove extraneous solid and colloidal particles. After filtration the solutions were overheated at 65 °C. Then the temperature of solution was reduced to 5 °C higher than saturation point and then the seed was *Z*-cut (one is point seed and one is large crystal plate) placed into the solutions. The temperature was reduced to a critical value of super cooling and the seed crystal began to grow upwards. The grown crystals are shown in Fig. 2.

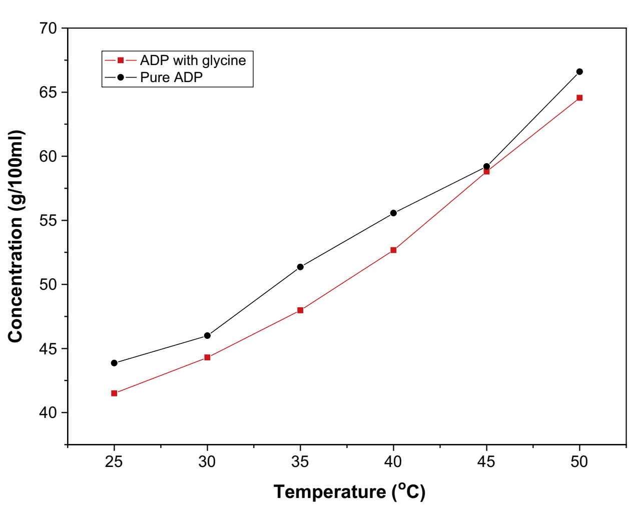

Fig. 1. Solubility of pure and 1 mol% of glycine doped ADP.

3. Characterization

3.1. UV–Vis spectroscopy

Crystal plates of pure and 1 mol% of glycine doped ADP were cut and polished at face (100) without any coating for optical measurements. In both the pure and doped ADP crystals the dimensions of the used crystals are $10 \times 10 \times 5\ mm^3$. Optical transmission spectra were recorded for the crystals in the wavelength region from 200 to 1100 nm using Perkin–Elmer Lambda 35 UV–Vis spectrometer. The recorded UV–Vis spectra are shown in Fig. 3.

It is observed from the figure that the 1 mol% of glycine doped ADP shows 75% of transmittance. In order to confirm the reproducibility, several times the beam was passed through the various regions of the crystals and the same results were observed. The pure ADP has 65% transmittance [12–14]. The large transmission in the entire visible region enables it to be a good candidate for electro-optic and NLO applications [15]. ADP and KDP crystals grown from deuterium show more than 80% of transparency in

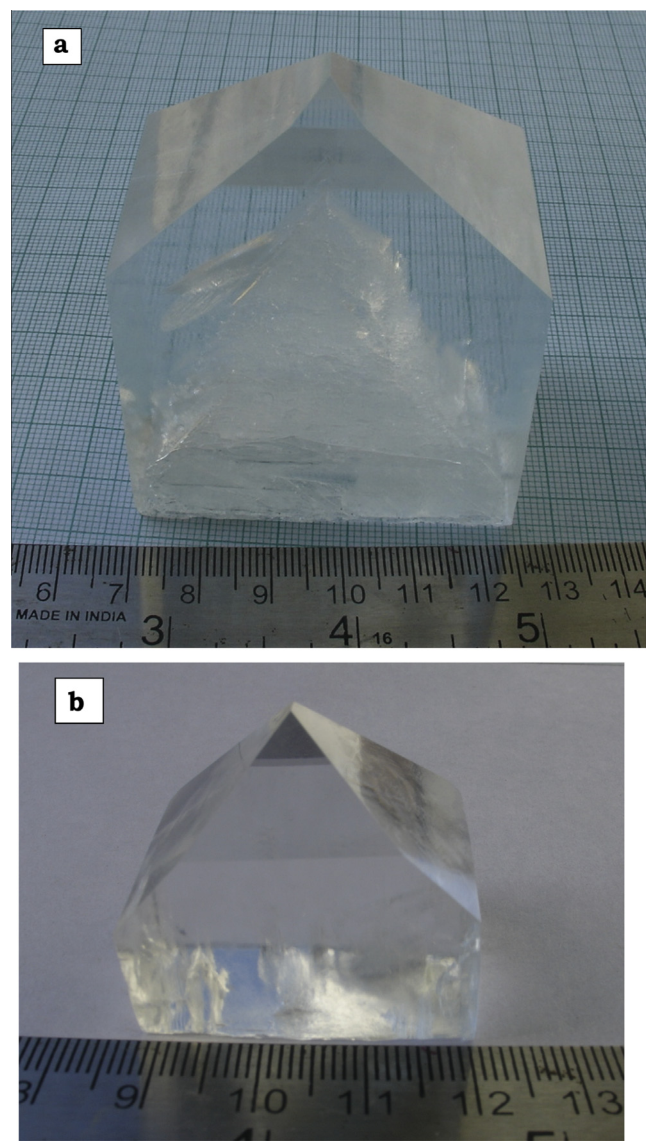

Fig. 2. 1 mol% of glycine doped ADP crystal grown by slow cooling along with seed rotation method using (a) big seed and (b) point seed.