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Comparative Studies on Structural, Mechanical, Optical and Laser Damage Threshold Studies on Ammonium Acid Phthalate Crystal Grown by Conventional and SR Grown Crystals

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Abstract

Objectives: The Sankaranarayanan–Ramasamy (SR) method is used to create high-quality, transparent ammonium acid phthalate (AAP) single crystals. Their structural, optical, mechanical, and electrical properties are then examined and compared to those of crystals grown using traditional methods. **Methods:** Using the SR approach, AAP crystals measuring 55 mm in length and 18 mm in diameter were formed from aqueous solution in the <001> direction. Single crystal X-ray diffraction (SCXRD) was used to estimate the unit cell characteristics, indicating an orthorhombic system with space group Pbca. The crystalline perfection was evaluated using high-resolution X-ray diffraction (HRXRD). Z-scan and UV-Vis transmittance spectroscopy were used to analyze optical characteristics. Mechanical property assessments, photoconductivity studies, and laser damage threshold testing were additional characterizations. **Findings:** HRXRD showed that the SR-grown AAP crystals (12.5″) had better crystalline perfection than those that were generated (15″) conventionally. SR-grown crystals had improved 10 % of transparency and nonlinear optical performance, according to optical analysis. These crystals also demonstrated enhanced mechanical strength, enhanced photoconductivity, and greater laser damage thresholds. **Novelty:** This study demonstrates how well the SR technique produces large, superior AAP single crystals with improved physical characteristics. The SR method's potential for sophisticated optoelectronic and laser applications is highlighted by the comparison with conventionally produced crystals.

Keywords: X-ray diffraction; Solution growth technique; High resolution X-ray diffraction; Single crystal X-ray diffraction (SCXRD)

1 Introduction

The outstanding nonlinear optical (NLO) characteristics of organic crystals have made them attractive options for photonic and optoelectronic applications. Electro-optic modulation, frequency doubling, frequency mixing, optical storage, and optical communications are among their many applications. Second-order nonlinear optical responses are amplified when organic molecules have electron-rich (donor) and electron-deficient (acceptor) substituents, which cause asymmetric charge distributions[1]-[2]. High phase-matchable NLO coefficients, broad optical transparency, chemical stability, and high laser damage thresholds are among the strict requirements that NLO crystals must meet in order to be feasible for real-world uses[3]–[4]. Extending benzene derivatives has been shown to significantly increase hyperpolarizability by increasing the π-electron density and delocalization length. A variety of photo-responses, such as photoluminescence, photoconductivity, photovoltaic behavior, and photocatalysis, are also displayed by organic molecules having delocalized π-electrons[5]. In particular, phthalate-based organic crystals are well suited for intra-laser modulation and acousto-optic devices due to their exceptional piezoelectric coefficients and acousto-optical interactions[6]. Furthermore, because of their affordability, mechanical pliability, and simplicity of cleavage, these materials are commonly used as diffracting elements in tiny spectrographs.

Although solution-based methods offer several benefits, producing high-quality phthalate crystals is still quite difficult. Solvent inclusions and uneven crystal shape are common problems with conventional solution (CS) growth techniques such solvent evaporation and sluggish cooling. The optical and mechanical performance of the crystal is significantly impacted by these flaws, making it less than ideal for sophisticated applications[7]-[8].

While phthalate-based crystals have been shown to be useful in a number of studies, nothing has been done to compare the structural and functional characteristics of crystals generated utilizing various solution-based growth techniques. The quality, optical characteristics, and photoconductivity of ammonium acid phthalate (AAP) crystals generated using the Sankaranarayanan–Ramasamy (SR) method vs the standard solution (CS) method are specifically not well-documented. Finding a dependable growing technique that produces crystals with exceptional structural integrity, optical transparency, and mechanical resilience is essential to utilizing AAP crystals to their full potential in NLO and photonic applications.

This work proves that the Sankaranarayanan–Ramasamy (SR) method is an excellent crystal growth methodology for creating big, superior single crystals of ammonium acid phthalate (AAP) with greatly improved optical and physical characteristics. High-Resolution X-ray Diffraction (HRXRD) research shows that, in contrast to traditional growth techniques, the SR approach promotes the development of bulk crystals with well-defined morphology, fewer microstructural flaws, and high lattice perfection. These SR-grown crystals are perfect for high-power laser systems and nonlinear optical applications because of their enhanced mechanical hardness, excellent optical transparency, and increased resistance to laser-induced damage. The SR approach represents a significant breakthrough in the synthesis of organic nonlinear optical materials and photonic devices by reliably growing large, defect-minimized AAP crystals.

2 Methodology

2.1 Slow Evaporation Solution Growth Technique

The analytical grade of ammonia solution and phthalic acid were taken in equimolar ratio and the calculated amount of material was dissolved in deionized water with the resistivity of $18.2\ \mathrm{M\Omega/cm}$ at room temperature. The reaction mechanism is depicted in Figure 1. After 25 days of growth, a good quality and well faceted single crystal was harvested from the mother solution with the dimension of $12 \times 10 \times 5\ \mathrm{mm}^3$. The grown AAP crystals were harvested when they attained an optimal size and shape. The grown crystals are optically transparent and non-hygroscopic. The grown crystal of AAP is shown in Figure 2(a) and the morphology is shown in Figure 2(b) and it was indexed using Enraf Nonius CAD4 diffractometer equipped in the graphite monochromated MoKα radiation ($\lambda = 0.71073\text{Å}$).

2.2 Sankaranarayanan-Ramasamy (SR) Method

The seed crystals collected from the conventional slow solvent evaporation technique were used for the unidirectional growth[9]. A suitable seed crystal cut along (001) plane with size of $5 \times 5 \times 3\ \mathrm{mm}^3$ was selected for single crystal growth. The ampoule was carefully designed to avoid growth of other faces. The seed crystal was mounted in the 18 mm diameter and 300 mm length ampoule. The growth ampoules were carefully mounted with individual seed having the plane (001) facing the saturated solution of AAP. Three times recrystallized materials were used in this growth. The glass ampoule was filled with saturated solution and porously sealed. The crystallizer was kept in a water bath to avoid the temperature fluctuation of the daily variation. The temperature of the top and bottom portion was set at 38°C and 33°C respectively.

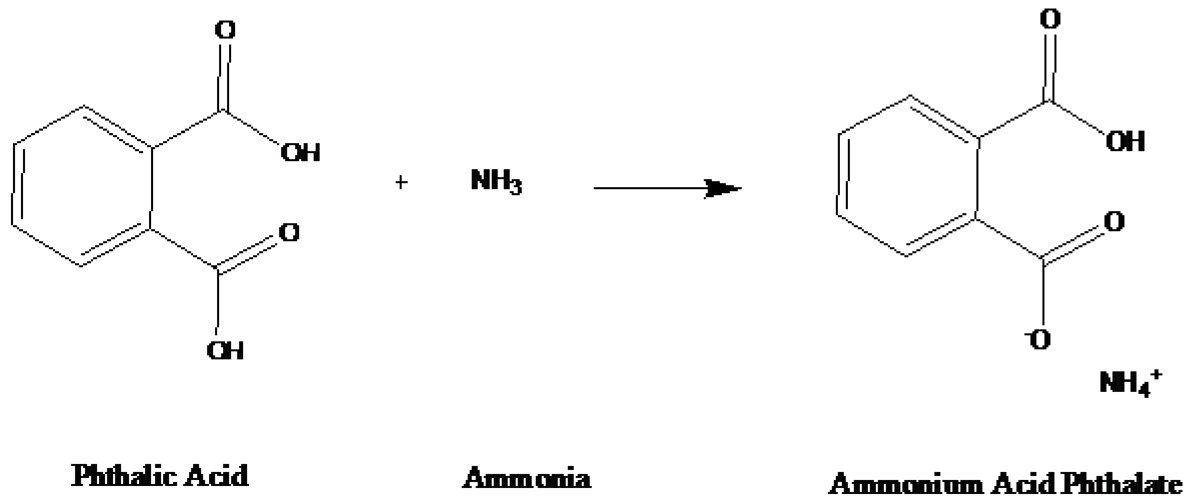

Fig 1. Reaction scheme of AAP

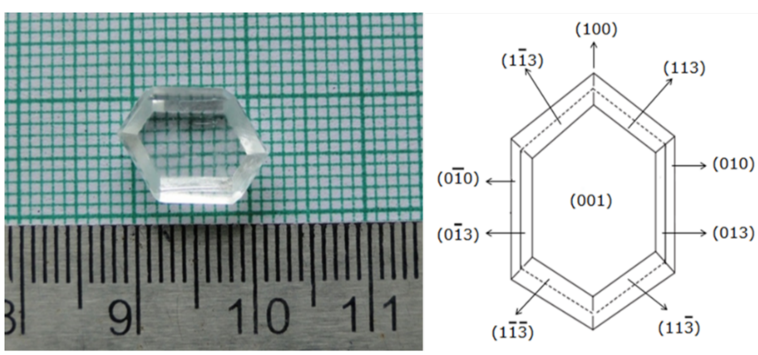

Fig 2. (a) Conventional slow evaporation grown AAP and its (b) Morphology

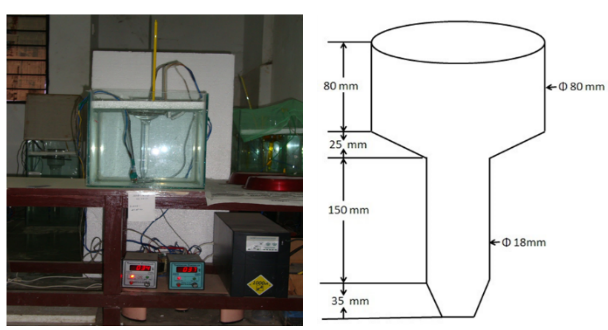

Fig 3. (a) SR crystal growth system (b) Schematic of SR glass ampoule

In conventional solution method a large quantity of solution in a 2 litre crystallizer is used and only small portion of synthesized solute is converted in to a AAP crystal. But, in SR method the solution was kept in a growth ampoule and the AAP thin plate as a seed crystal was exposed to the solution. The entire quantity of the solute was converted into crystal thus achieving solute-crystal conversion efficiency of nearly 100 percent. Cleaved SR grown crystals are shown in Figure 4.

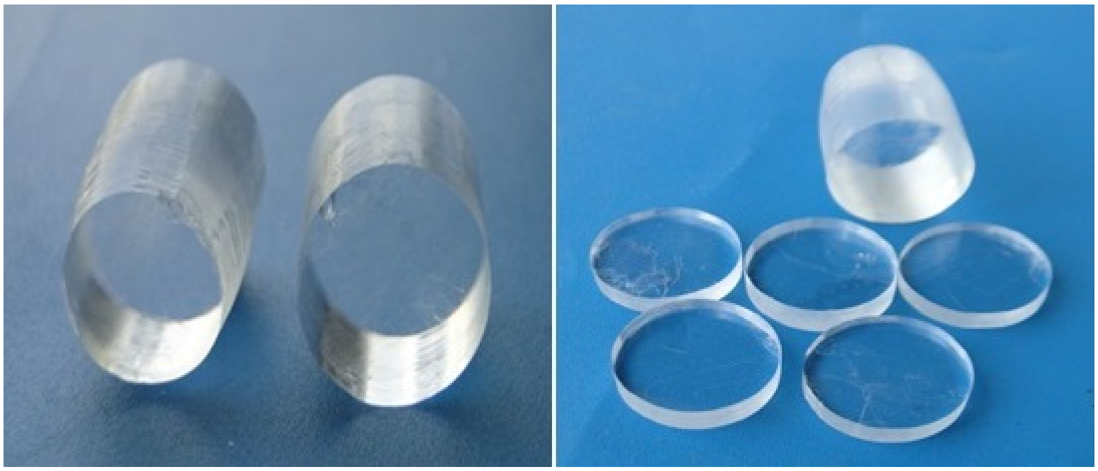

Fig 4. Cleaved SR grown crystals

3 Results and Discussion

3.1 HRXRD Studies

Figure 5 shows the high-resolution rocking/diffraction curves (DC) recorded for a typical AAP crystal grown by conventional and SR method using (114) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer with CuKα_1 radiation. As seen in the figure, the DC contains a single peak and indicates that the specimen is free from structural grain boundaries. The Full Width at Half Maximum (FWHM) of the curve is 15" for conventional grown AAP crystal. The much broadness with good scattered intensity along both the wings of the DC indicates that the crystal contains both vacancy and interstitial type of defects [10]. The FWHM of the curve is 12.5" for SR grown AAP. The single sharp diffraction curve with very low FWHM indicates that the crystalline perfection is quite good without having any internal structural grain boundaries. The SR method grown crystal show good crystalline perfection compared to conventional method grown crystal.

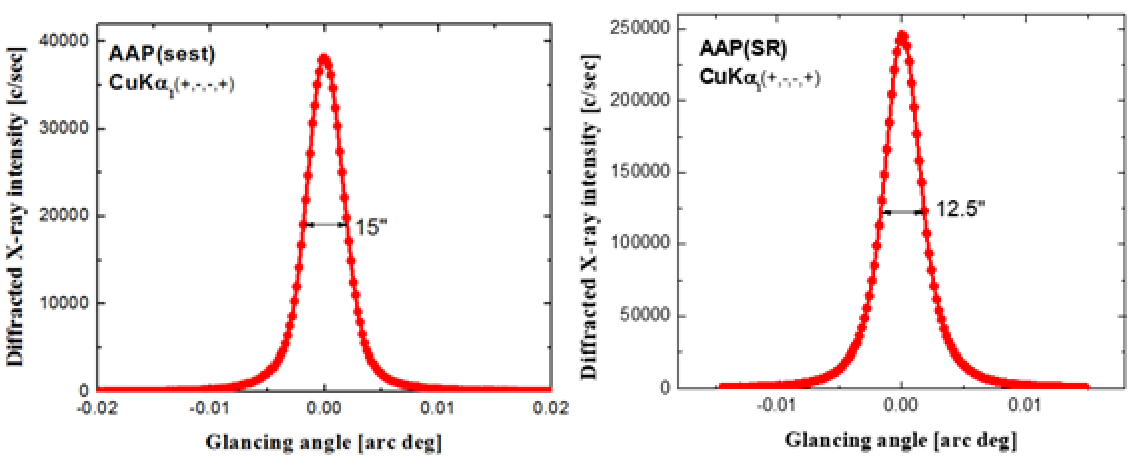

Fig 5. Rocking curves of AAP crystal grown by a).Conventional method b) SR method

3.2 Laser Damage Threshold Studies

Using a Nd:YAG laser, the laser damage threshold value of the as-grown AAP crystal was determined. Numerous laser characteristics, including wavelength, energy, pulse duration, longitudinal and transverse mode structure, beam size, beam location, etc., affect the laser damage threshold [11]. The AAP crystal sample was placed on an X-Y translator for the multiple shot experiment, which makes it easier to accurately expose different parts of the sample. Both visible damage and audible cracking indicate the beginning of damage. The laser damage threshold of AAP crystal was measured using a fundamental wavelength of 1064 nm, a pulse width of 10 ns, and a repetition rate of 10 Hz. The laser beam of diameter 4 mm was focused on the crystal. Laser beam was focused on the crystal with a 20 cm focal length convex lens and the crystal was placed just at the focal point. An attenuator was used to vary the energy of the laser pulses with a polarizer and a half wave plate. The energy of each shot was measured using the combination of phototube and oscilloscope. The damage threshold of the crystal was calculated using the expression, (Pd) $= \mathrm{E}/\tau\pi r^2$ where E is the input energy (mJ), τ is the pulse width (ns) and r is the radius of the spot (mm). The comparative characterizations have been made on conventional and SR method grown AAP crystals. AAP is highly cleavable along plane (001). Identical thickness samples were prepared (by cleaving) from both conventional and SR grown crystals and used for the measurement (No polishing was done). In order to confirm the reproducibility, every input energy was repeated several times, and the similar results have been observed. The bulk damage results are presented in Figure 6. Laser damage threshold 1.0 (conventional) and 1.5 (SR) J/cm2 show that SR grown AAP possesses higher laser stability than conventional grown AAP.

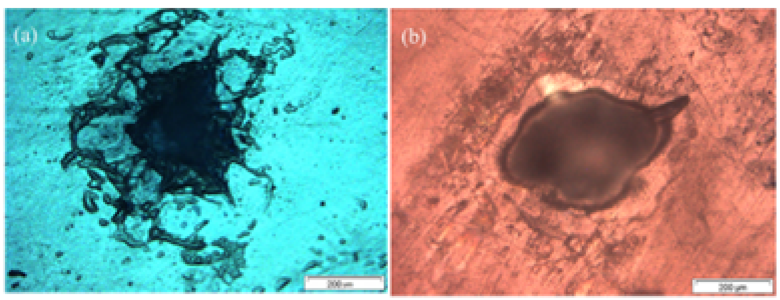

Fig 6. Damage obtained in the (a) conventional and (b) SR method grown crystal during laser damage threshold studies

3.3 UV-Vis Studies

The Perkin-Elmer Lambda 35 spectrophotometer was used to record the optical absorption spectra between 200 and 1100 nm in wavelength. The measurement is made using a 2 mm thick crystal that has not been polished or coated with antireflection material. With a lower cutoff wavelength of about 300 nm, AAP offers adequate transmittance throughout the visible and near-infrared spectrums [12]. Figure 7a displays the observed transmission spectra of AAP single crystals produced using the traditional and SR methods. The clarity of the AAP crystal generated by the Sankaranarayanan–Ramasamy method is 10% greater. This is because, in comparison to traditional solution-grown crystals, unidirectionally grown crystals may have fewer flaws, which reduces the scattering centers in the crystals and raises the output intensity.

3.4 Microhardness Studies

Figure 7b depicts the variation in hardness number (Hv) as a function of applied load. The figure clearly shows that the hardness number (Hv) increases with increasing load, and small cracks were detected for AAP beyond 25 g. It could be caused by the discharge of internal stress. Beyond 25 g, SR produced AAP crystals show fewer fractures. The increased mechanical hardness will have a substantial impact on device applications. The graph shows that the hardness value for SR method created crystals is higher than that of traditional method grown crystals. The enormous stress necessary for uniform dislocation nucleation in the small dislocation-free area indented is responsible for the majority of hardness [13]. Therefore, a higher hardness value for a crystal formed using the SR method signifies a higher stress needed to create a dislocation, confirming more crystalline perfection. Even if cracks start to appear for both crystals at the same stress, the SR method-grown crystal was found to be more affected by crack formation in terms of hardness decrease.

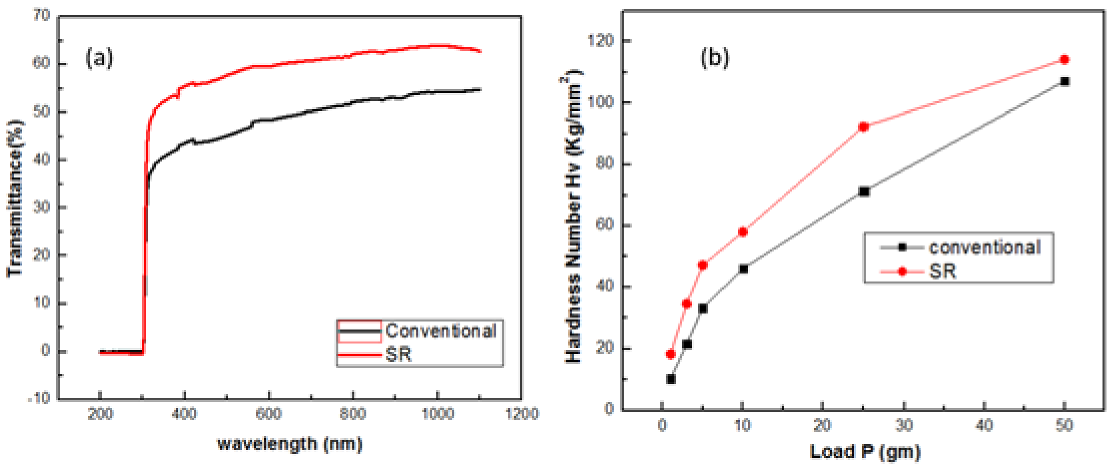

Fig 7. a) UV- Transmittance spectrums of conventional and SR grown AAP single crystal b) Variation in hardness number (Hv) as a function of applied load

3.5 Photoluminescence Studies

Figure 8 displays the field dependency of the photocurrent and dark currents of conventional and SR-grown ammonium acid phthalate crystals. Photocurrent appears to be lower than the dark current for the same applied field for both conventional and SR produced ammonium acid phthalate crystals; this phenomenon is known as negative photoconductivity. It's possible that the sample's negative photoconductivity results from fewer charge carriers when exposed to radiation [(12)],[(13)],[(14)]. The Stockmann model explains why mobile charge carriers diminish during negative photoconductivity [(15)]-[(16)]. Dislocation is the primary cause of the higher dark current and higher photocurrent in the AAP crystal generated using the traditional approach as opposed to the SR formed crystal.

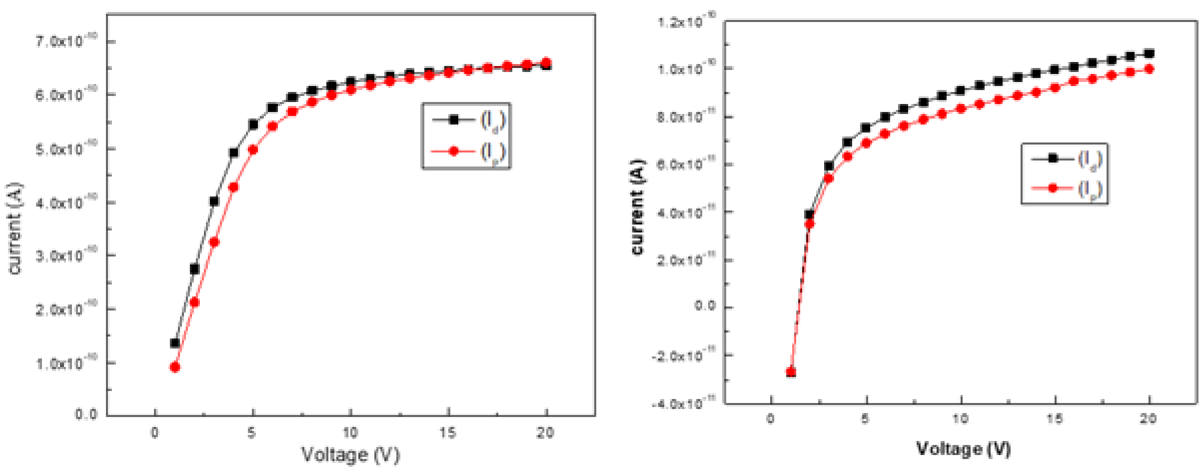

Fig 8. Field dependent conductivity of a) conventional and b) SR Grown AAP single crystal

4 Conclusion

Good optical quality single crystals of organic Ammonium Acid Phthalate (AAP) were grown by slow solvent evaporation technique. <0 0 1> directed ammonium acid phthalate (AAP) single crystal with 55 mm length and 18 mm diameter has been grown by the Sankaranarayanan–Ramasamy method. Full width at half-maximum value of the Sankaranarayanan–Ramasamy method grown AAP crystal, which is 12.5 arc deg, shows that the crystalline perfection is good. The AAP crystal grown by

Table 1. Comparative measurements of conventional and SR method grown AAP crystal along <001> direction

Name of the studies	SEST grown AAP	SR grown AAP
HRXRD – FWHM	15”	12.5”
Laser Damage Threshold	1.0 J/cm^2	1.5 J/cm^2
Microhardness at 1 g at 50 g	10.3 kg/mm^2 107.2 kg/mm^2	18.8 kg/mm^2 124.5 kg/mm^2
UV-Vis NIR	50%	60%
Z- scan	Scattered	Output has been measured
Photoconductivity	I_p = 6.55223x10^{-10} I_d = 6.60891x10^{-10}	I_p = 9.98649x10^{-11} I_d = 1.06342x10^{-10}

the Sankaranarayanan–Ramasamy method has 10% higher transmission. The laser damage threshold has been measured and the observed value of SR method grown AAP crystal is higher than that of conventional slow evaporation method grown crystal. The crystal grown by SR method has higher hardness value than conventional method grown crystal. The two-photon absorption coefficient and third order nonlinear optical susceptibility were calculated by Z-scan technique and affirm that SR grown AAP crystal exhibits the nonlinear optical properties. The photocurrent was less than the dark current, signifying negative photoconducting nature. It is also observed that values of dark and photo current of conventional grown AAP crystal is less than SR grown AAP crystal. Comparative measurements of conventional and SR method grown AAP crystal along <001> direction is shown in Table 1.

The improved laser damage threshold and optical clarity suggest that SR-grown AAP crystals can be integrated into acousto-optic modulators, frequency doublers, or UV-transparent windows. Prototype development for optical switching and photonic circuits could be explored. In conclusion, the SR process creates a way to produce premium organic crystals, such as AAP, with specific qualities for cutting-edge uses. The current study lays the groundwork for future advancements in nonlinear optics, crystal engineering, and the production of photonic devices in addition to reaffirming the benefits of the SR approach.

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