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Studies on the growth and physical properties of nonlinear optical crystal: 2-Amino-5-nitropyridinium-toluenesulfonate

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ABSTRACT

Single crystals of 2-amino-5-nitropyridinium-toluenesulfonate (2A5NPT) were grown by the slow cooling method. The unit cell dimensions were determined from single crystal X-ray diffraction studies. The thermal parameters – thermal diffusivity (α), thermal effusivity (e), thermal conductivity (K) and heat capacity (C_p) of 2A5NPT were measured by an improved photopyroelectric technique at room temperature. Single and multiple shot experiments performed on the grown crystals for the second harmonic of pulsed Nd:YAG laser (532 nm) show that it exhibits a high laser damage threshold which is a favorable property for nonlinear optical applications. Dielectric constant and dielectric loss of the grown crystal were evaluated for the frequency range 1 kHz–1 MHz in the temperature region 40–130 °C. Hardness values were measured using Vickers hardness measurement.

1. Introduction

Organic crystal exhibiting nonlinear optical effects have been explored with a view to developing optical devices, for example optical modulators and frequency-doubling devices [1]. But these are generally difficult to grow as large single crystals owing to the weak van der Waals and/or hydrogen bonds [2–6]. Also, the softness of the crystal makes them less advantageous from a device point of view compared to inorganic crystals. Considerable effort is being made to find new materials that have the optimal characteristics needed for use as a nonlinear optical (NLO) element [7]. Masse et al. have published a series of organic–inorganic crystals of 2-amino-5-nitropyridine (2A5NP) and inorganic acids such as arsenic acid, which were designed for NLO materials. 2A5NP allows for the growth of numerous salts, like 2-amino-5-nitropyridinium dihydrogen phosphate, 2-amino-5-nitropyridinium dihydrogen arsenate, 2-amino-5-nitropyridinium acetophosphate, 2-amino-5-nitropyridinium chloride (2A5NPCl), 2-amino-5-nitropyridinium bromide (2A5NPBr) and 2-amino-5-nitropyridinium-L-monohydrogentartrate (2A5NPLT) [8–11]. 2A5NPT is a potential nonlinear optical crystal which is reported to exhibit second harmonic efficiency 90 times that of the widely used inorganic crystal, potassium dihydrogen phosphate at the fundamental wavelength of 1064 nm [12]. This organic material crystallizes in the monoclinic crystal system with noncentro symmetric space group *Pc*, and the unit cell parameters are $a = 11.529(5)$ Å, $b = 7.914(7)$ Å, $c = 15.213(5)$ Å, and $\beta = 92.10(3)^\circ$ [12]. The crystal structure consists of 2-amino-5-nitropyridinium and toluenesulfonate molecules held together by a network of hydrogen bonds resulting in two-dimensional hydrogen bond framework. Single crystals of 2A5NPT of reasonable size are grown from solution of 2A5NPT by slow cooling technique. The synthesis, growth details, and preliminary characterization of this crystal have already been reported elsewhere [12], however optical quality of the crystals was poor. In this work, single crystals of 2A5NPT have been grown from saturated solution of the synthesized salt of 2A5NPT by the cooling technique using mixed solvent of methanol and dimethyl formamide as solvent. In this paper, we report bulk growth, laser induced surface damage threshold, dielectric properties and Vicker's micro hardness of the grown crystals. The thermal transport properties, namely thermal diffusivity (α), thermal effusivity (e), thermal conductivity (K) and heat capacity (C_p) of 2A5NPT single crystal are measured using an improved photopyroelectric (PPE) technique.

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2. Experimental procedure

2.1. Material synthesis

The commercially available 2A5NP (Merck, purity >98%) is a weak Bronsted base and can acquire a proton in a strongly acidic aqueous medium (pH < 2). This induces the dissolution of this molecule in an aqueous acidic medium by forming the $2A5NP^{+}$ cation and leads to the synthesis of hydrogen – bonded salts with the conjugated bases of strong or medium acids. The organic–organic 2-amino-5-nitropyridinium-toluenesulfonate salt is obtained by dissolving the 2A5NP in p-toluenesulfonic acid at 50 °C in millipore water of resistivity 18.2 MΩ cm.

2.2. Crystal growth

In this investigation single crystals are grown by slow cooling technique using mixed solvent of methanol and dimethyl formamide as solvent under controlled thermal environment. Small, optically clear crystal grown by slow cooling method is used as seed to grow larger single crystal in a beaker. A programmable PID temperature controller (Eurotherm, Model 3216) with the lowest cooling rate of 0.01 °C/h is employed for the slow cooling process. In all the growth runs, a cooling rate of 0.01 °C/h is adopted. Transparent single crystals of dimensions up to $10 \times 10 \times 8\ mm^3$ could be grown from 200 ml of solution in about 30 days. Fig. 1 shows as grown crystals of 2A5NPT. The grown crystals are inclusion free and chemically stable.

3. Characterization

The grown crystals were subjected to X-ray diffraction studies using Nonius CAD4/MACH 3 single crystal X-ray difffractometer, using Mo Kα (λ = 0.71073 Å). An improved photopyroelectric (PPE) technique was used to determine the thermal transport properties of the crystals. The 2A5NPT has no phase transition before melting, as is evident from TG/DTA analysis (NETZSCH STA 409) performed in the temperature range 30–600 °C. So these measurements were limited to room temperature only. A detailed description of the experimental set up and the method to determine the thermal parameters of crystals by this technique have been reported elsewhere [13]. In order to obtain good uniform surface finish, each crystal having thickness < 2 mm was carefully polished using a polishing sheet. In order to enhance its optical absorption, a very thin layer of carbon black from a benzene flame was carefully coated onto the surface of the prepared samples to be illuminated. In this measurement, a thermally thick polyvinylidene difluoride (PVDF) film with thickness 28 μm, coated with Ni–Cr on both sides, with a pyroelectric coefficient $P = 0.25 \times 10^{-8}\ V\ cm^{-1}\ K^{-1}$, was used as the pyroelectric detector. The thermally thick pyroelectric detector film was attached to one side of the sample, which was also thermally thick, and the combination was mounted on a thermally thick backing medium made of a copper plate. The other side of the sample was illuminated with an intensity modulated beam of light, which gave rise to periodic temperature variations by optical absorption. The thermal waves so generated propagated through the sample and were detected by the pyroelectric detector. A 120 mW He–Cd laser of wavelength 442 nm, intensity modulated by a mechanical chopper, was used as the optical heating source. The sample-detector-backing assembly was enclosed in a chamber, and was kept at room temperature (28 °C). The signal output was measured with a lock-in amplifier (Stanford Research Systems, Model: SR830) with 10 MΩ input impedance and 50 pF input capacitance. The frequency of modulation of the laser source was kept in the range 60–80 Hz to ensure that the detector, the sample and the backing medium were all thermally thick during measurements. The thermal thickness of each sample in this experiment was estimated by plotting the PPE amplitude and phase with frequency at room temperature. Measurement of the PPE signal phase and amplitude enabled us to determine the thermal diffusivity (α) and thermal effusivity (e) of the sample. From these measured values of α and e, thermal conductivity (K) and heat capacity (C_p) were evaluated.

A Q-switched Nd:YAG (yttrium aluminum garnet) Innolas laser of pulse width 7 ns and 10 Hz repetition rate operating in TEM_{00} mode is used as the source. The energy per pulse of 532 nm laser radiation attenuated using high energy variable attenuator is measured using an energy power meter (Scientech Inc.) which is externally triggered by the Nd:YAG laser. Since the surface damage is affected by the energy absorbing defects such as polishing contaminants and surface scratches, which get incorporated during mechanical polishing, all the experiments are performed on the highly polished crystals (uniformly polished with high quality polishing powder) thus minimising the strain and incorporation of impurities. For both single and multiple shot experiments, the sample is mounted on an X–Y translator which facilitates in bringing different areas of the sample for exposure precisely. For surface damage, the sample is placed at the focus of a plano-convex lens of focal length 80 mm. The onset of damage can be determined by visual damage and audible cracking.

The capacitance (C_{crys}) and dielectric loss (tan δ) were measured using the conventional parallel plate capacitor method with frequency range (1 kHz–1 MHz) using Agilent 4284A LCR meter at various temperatures ranging from 323 K to 403 K.

The load dependence of Vickers microhardness is measured on plate of 2A5NPT. Microhardness indentations are made on 2A5NPT crystal plates of thickness 3 mm using SHIMADZU HMV-2000 for loads varying from 10 to 70 g. The indentation time is maintained constant at 10 s.

4. Results and discussion

From the single crystal X-ray diffraction studies, it is observed that the crystal belongs to the monoclinic system with the space group of *Pc* and the unit cell parameters are a = 11.529(5) Å, b = 7.914(7) Å, c = 15.213(5) Å, and β = 92.10(3)° [12]. The thermal properties of crystals are of basic importance, and are relevant for various applications. When a laser beam passes through the crystal, part of the light will be absorbed by

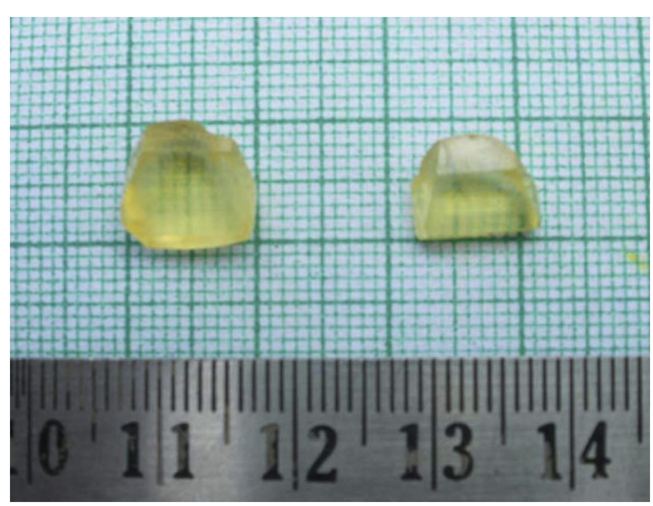

Fig. 1. Grown single crystals of 2A5NPT.

the crystal and get converted into heat, forming a temperature gradient and resulting in consequent thermal expansion. If the thermal expansion coefficients of the crystal are anisotropic, the crystal may crack when a high enough thermal energy gets deposited due to high intensity of the incident light. A crystal with a high specific heat will have a lower temperature gradient than a crystal with a low specific heat while absorbing the same quantity of heat.

The thermal conductivity of 2A5NPT is comparatively higher than the inorganic crystals potassium dihydrogen phosphate (KDP), ammonium dihydrogen phosphate (ADP), beta-barium borate (BBO) and lithium iodate ($LiIO_3$). Table 1 shows the thermal parameters of 2A5NPT and a few other known crystals [14–21]. The specific heat of a crystal is a basic property that is important for device applications. If a crystal possesses a large specific heat, it may have large damage threshold. The C_p of the 2A5NPT crystal is 1283 J kg^{-1}K^{-1} and is comparatively higher than the well known inorganic crystals potassium dihydrogen phosphate (KDP), ammonium dihydrogen phosphate (ADP), beta-barium borate (BBO) and lithium iodate ($LiIO_3$). This suggests that the 2A5NPT could exhibit more resistance to damage caused by laser irradiation.

For harmonic generation, the efficiency of conversion is strongly dependent on the incident power level. The operation of nonlinear optical devices obviously involves the exposure of these materials to high intensity laser light. Hence, the utility of NLO crystal depends not only on the linear and nonlinear optical properties but also largely on its ability to withstand high power lasers [22]. The knowledge of laser damage studies on NLO crystals is extremely important in NLO applications. Single shot and multiple shot (30 pulses) surface laser damage thresholds are determined to be 54.92 GW/cm^2 and 41.19 GW/cm^2 respectively at 532 nm laser radiation. Fig. 2(a) and (b) shows the optical micrograph of the single shot damage profile of 532 nm laser radiation of 2A5NPT. The damage pattern of 2A5NPT (Fig. 2) shows blobs surrounding the core of the damage. Such blobs are generally seen in crystals where the damage is mainly due to thermal effects resulting in melting and solidification or decomposition of the material [22]. Recent investigations into laser damage in various optical materials by nanosecond pulses have shown that the temperature reached at the damage site could be as high as 12,000 K [23]. Since 2A5NPT decomposes at around 204 °C it is most likely that in the present case damage occurs due to decomposition of the crystal. Hence, in 2A5NPT we can expect the damage to be of thermal origin. However, one cannot rule out other mechanisms being operative simultaneously, as the damage mechanism is quite complex and depends on the nature of the material and various experimental parameters.

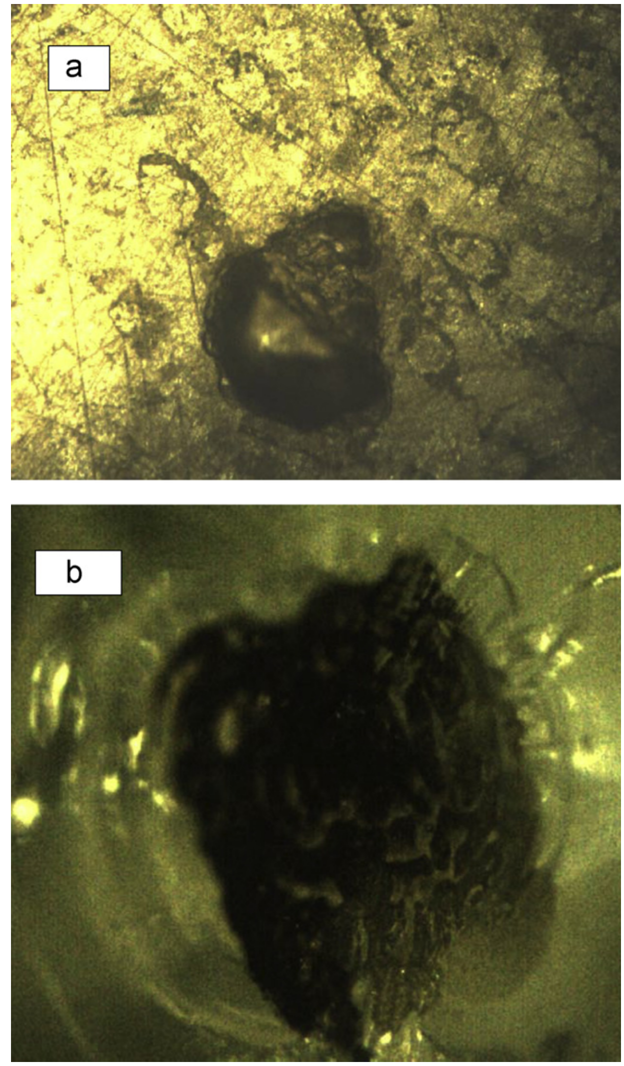

Fig. 2. (a) and (b) Laser damage profiles of 2A5NPT.

Table 1
Comparison of the thermal parameters of 2A5NPT with a few known crystals.

Sample	Thermal effusivity (e) (W s$^{1/2}$/m^2 K)	Thermal diffusivity (α) ($\times 10^{-6}$ m^2/s)	Thermal conductivity (K) (W/mK)	Specific heat capacity (C_p) (J/kg K)
Literature [14–21]				
KDP	–	–	1.21 (302 K)	857 (298 K)
DKDP	–	–	1.86	–
ADP	–	–	1.26 (315 K)	1236 (298 K)
KTP	–	–	2	688
BBO	–	–	1.20	490 (298 K)
$LiIO_3$	–	–	1.47	365
LAP	–	–	0.59	–
EMPO	660	2.773	1.099	443
BEDO	669	3.131	1.185	322
EDMP.3H_2O	661	1.744	0.873	716
MDMP.3H_2O	663	1.804	0.891	706
DMAPDP	663	2.951	1.140	332
2A5NPT (Present study)	3216	2.561	5.143	1283

Abbreviations: KDP, potassium dihydrogen orthophosphate; DKDP, deuterated potassium dihydrogen phosphate; ADP, ammonium dihydrogen orthophosphate; KTP, potassium titanyl phosphate; BBO, beta-barium borate; $LiIO_3$, lithium iodate; LAP, L-arginine phosphate monohydrate; EMPO, 3-[(1E)-N-ethylethanimidoyl]-4-hydroxy-6-methyl-2H-pyran-2-one; BEDO, bis-2,7-diethylaminohepta-2,5-dien-4-one; EDMP·3H_2O, 1-ethyl-2,6-dimethyl-4(1H)-pyridinone trihydrate; MDMP·3H_2O, 1-methyl-2,6-dimethyl-4(1H)-pyridinone trihydrate; DMAPDP, 4-dimethylaminopyridinium dihydrogen phosphate.

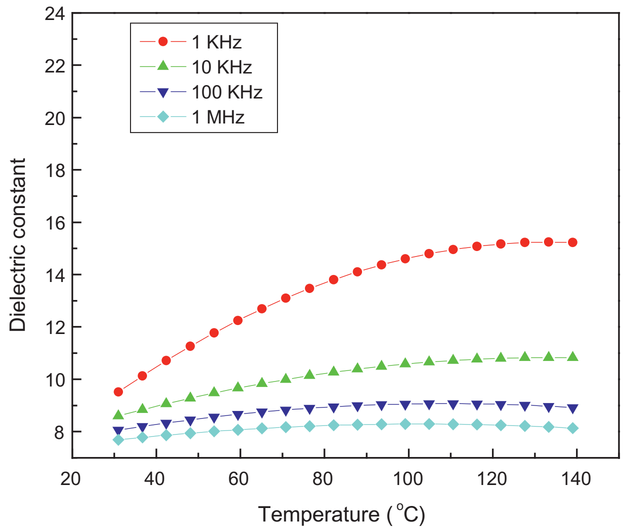

Fig. 3. Temperature dependence of dielectric constant of 2A5NPT for various frequencies.

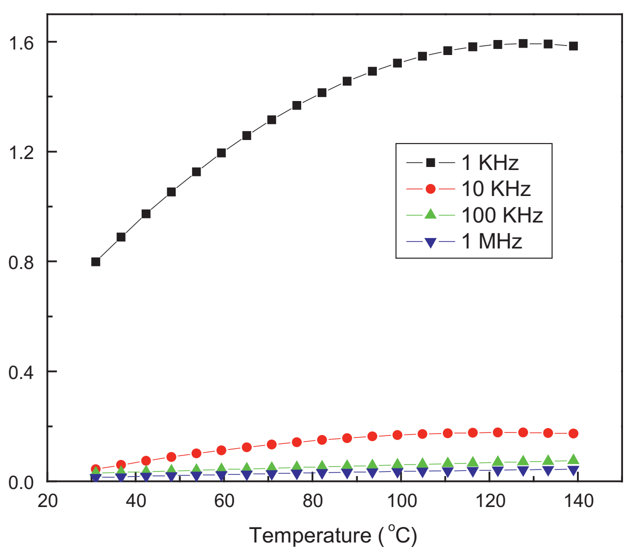

Fig. 4. Temperature dependence of dielectric loss of 2A5NPT for various frequencies.

The dielectric measurements are shown in Figs. 3 and 4. The low value of dielectric loss (tan δ) indicates that the grown crystals of 2A5NPT are of reasonably good quality. The dielectric constant of 2A5NPT crystal at 413 K is 15, and this value decreases to 9.5 at 303 K (for 1 kHz). The dielectric constant of dispersive medium decreases because the term contributing to dielectric constant from ion–dipole interactions is compensated by the thermal energy leading to the relaxation of polarization.

Information about the mechanical hardness of nonlinear optical crystals is important not only from the device point of view but also due to the close correlation between mechanical hardness, bond strength, laser damage, etc. [24–26]. Fig. 5 shows the load dependence of hardness of 2A5NPT. From the plot it is clear that Vickers hardness number (VHN) increases with load. The measurement performed beyond a load of 70 g resulted in severe cracks. This may be due to the release of internal stress generated locally by indentation. The increase in VHN at low loads can be attributed to the work hardening of surface layers. Similar load dependence is observed in other nonlinear optical crystals.

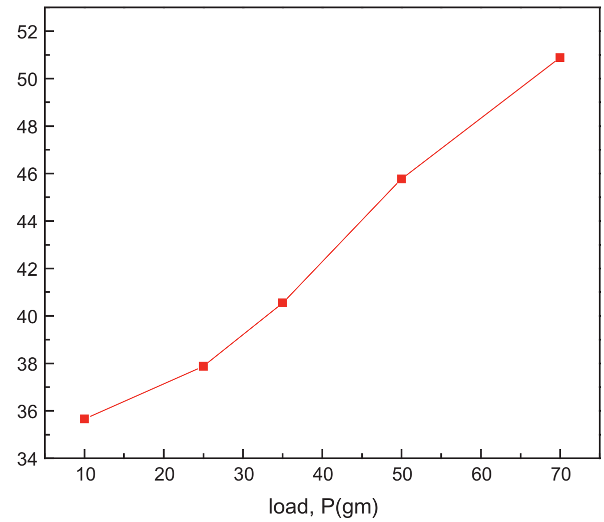

Fig. 5. Load dependence of Vickers hardness number of 2A5NPT.

5. Conclusion

Single crystals of 2A5NPT were grown from solution by the temperature-lowering method. The unit-cell parameters of 2A5NPT were confirmed by single crystal X-ray diffraction analysis. The laser induced surface damage threshold values of a recently developed nonlinear optical crystal, 2A5NPT, are reported. The single shot and multiple shot damage threshold experiments performed on the plate of 2A5NPT are evaluated as 54.92 GW/cm^2 and 41.19 GW/cm^2, respectively, for 532 nm Nd:YAG laser radiation. The high value of damage threshold is related to the specific heat of the crystal which is reasonably high. The measured thermal conductivity and heat capacity by photopyroelectric technique, suggest that the 2A5NPT may have high optical damage threshold value, which is an essential requirement for the fabrication of nonlinear optical devices. The dielectric constant and dielectric loss studies of 2A5NPT establish the normal behavior. From the mechanical measurements, it was observed that the hardness increases with increase of load.

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