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Organic nonlinear optical DAST crystals for electro-optic measurement and terahertz wave generation

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Abstract

We review the recent developments of crystal growth, electro-optic (EO) measurements and terahertz (THz) wave generation of organic nonlinear optical (NLO) 4-dimethylamino-*N*-methyl-4-stilbazolium tosylate (DAST). DAST crystals are expected to apply high-performance electric-field sensors, THz wave generators, and so on. We had developed a new technique called the slope nucleation method (SNM) for the growth of high-quality DAST crystals. Using SNM, we could effectively grow high-quality DAST crystals as compared to conventional spontaneous nucleation method. The EO sensitivity of DAST crystals depended on the crystal thickness and exhibited an increase of more than 45-fold that of the commercial $KTiOPO_4$ (KTP) crystals. The high-quality DAST crystals could also generate a coherent, widely tunable THz wave in the range of 2–31.5 THz by using the difference frequency generation (DFG) based on the KTP-optical parametric oscillator (OPO).

The authors also demonstrated the efficient crystallization by irradiating femtosecond laser pulse into the supersaturated solution. The laser irradiation increased the probability of nucleation. Aging the solution prior to laser irradiation could enhance the probability of nucleation. These results indicate that the laser irradiation could promote DAST nucleation in the supersaturated solution.

Keywords: Organic crystal; DAST; Electro-optic; Terahertz wave generation; Laser irradiation

1. Introduction

Organic nonlinear optical (NLO) materials have attracted much interest because of their large electro-optic (EO) coefficient, small dielectric constant, short-response time and large NLO properties. These properties are greatly superior to those of inorganic NLO materials. Among organic NLO materials, 4-dimethylamino-*N*-methyl-4-stilbazolium tosylate (DAST) [1,2], which is shown in Fig. 1, is a promising material due to its much larger EO coefficient ($r_{11} = 92 \pm 9$ pm/V at $\lambda = 720$ nm) [3], NLO properties ($d_{11} = 1010 \pm 110$ pm/V at $\lambda = 1318$ nm) [4] and lower dielectric constant ($\varepsilon = 5.2$) [3]. Furthermore, DAST is a relatively hard material due to ionic bonds in its structure. Accordingly DAST crystals are expected to apply for the high-sensitive electric-field sensor and the source of THz wave with high-power and broadband. High-quality DAST crystals are essential to fabricate the reliable applications. However, it is difficult to grow high-quality DAST crystals reproducibly. Therefore, we previously developed a novel growth technique called the slope nucleation method (SNM) [5]. The results of X-ray diffraction (XRD) rocking curve measurements indicated that the SNM is effective for growing high-quality DAST crystals as compared to conventional spontaneous nucleation method [5,6]. The EO sensitivity of DAST crystals depended on the thickness and exhibit an increase of more than 30-fold that of the commercial $KTiOPO_4$ (KTP) crystals with almost equal thick-

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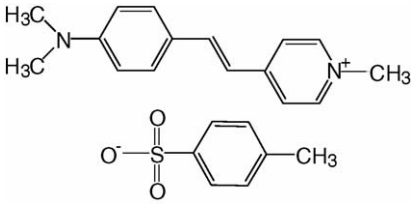

Fig. 1. Structure of DAST molecule.

ness [7]. The high-quality DAST crystals could also generate a coherent, widely tunable terahertz (THz) wave in the range of 2–31.5 THz by using the difference frequency generation (DFG) based on the KTP-optical parametric oscillator (OPO) [8]. The authors also demonstrated the efficient crystallization by irradiating femtosecond laser pulse into the supersaturated DAST solution. The femtosecond-laser irradiation increased the probability of DAST nucleation [9]. In this paper, we discuss the crystal growth, EO measurements, THz wave generation and the effect of femtosecond-laser irradiation into the DAST solution.

2. Experiments, results and discussions

2.1. Crystal growth

Large, high-quality DAST crystals were previously grown from a seed using slow cooling methods in methanol solvent. However, DAST crystals grown spontaneously showed better quality compared to that grown by the seed method [10]. Spontaneously nucleated DAST crystals, which tend to be planar shape with the (0 0 1) surface as the largest facet, usually develop on the bottom of the growth vessel and adhere the bottom. These phenomena make DAST crystallinity poor because of the mechanical stress on their surface. It would be ideal for the crystals to be grown in a state where the (0 0 1) facet is never in contact with the vessel; that is to say, to be grown in a state where the crystal is erect. To realize this condition, we developed a novel growth technique called the SNM [5]. In SNM, a Teflon plate with grooves was put into the growth solution (Fig. 2). Except for this point, the growth process is the same as in the case of conventional spontaneous nucleus growth. The nucleation and growth processes are described as follows: Small spontaneous nuclei are generated in the supersaturated solution and fall down onto the slope (Fig. 2(a)). As DAST crystals grow larger, they slip downward along the slope until they arrive at one of the grooves (Fig. 2(b)). Finally, the crystals stand; it means contact-free condition of the (0 0 1) facet, and then continue to grow larger on the groove (Fig. 2(c)). High-quality DAST crystals were thus effectively obtained by SNM. The SNM enables to control the nucleation position and the growth orientation of DAST crystals.

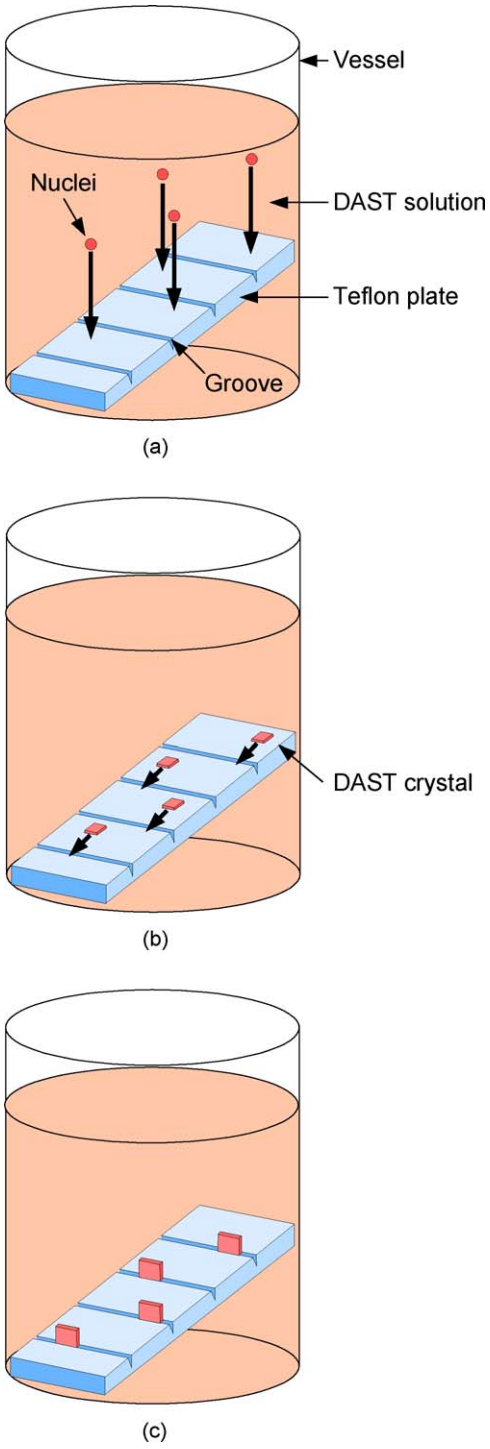

Fig. 2. Illustration of the SNM. The growth processes are described as follows: (a) spontaneous nuclei are generated in the supersaturated solution and fall down onto the Teflon plate. (b) As DAST crystals grow larger, they slip downward along the slope. (c) DAST crystals stand at the groove due to the inertial force of the slipping and continue to grow larger on the groove.

We measured the full-width at half-maximum (FWHM) of DAST (0 0 1) XRD rocking curve to evaluate crystallinity. Measurement was conducted on five samples for each type of DAST crystals. The FWHM of the DAST crystals grown by the SNM is 13–33 arcsec [6]. These values are much smaller than those grown by the conventional method without the slope, which range from 50 to 130 arcsec [5]. The best FWHM of the DAST (001) rocking curve (13 arcsec) is close to that of a commercial Si(1 1 1) wafer (10.4 arcsec). These results indicate that the SNM is effective for growing high-quality DAST crystals. We can also grow several high-quality DAST crystals simultaneously in one

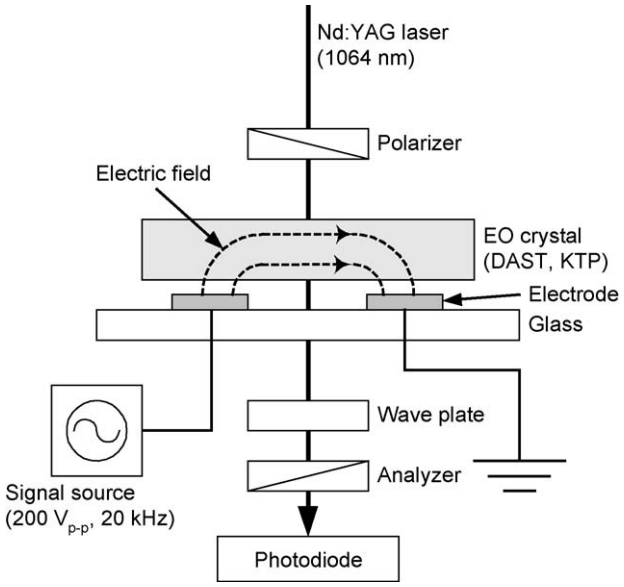

Fig. 3. Schematic illustration for the EO measurement of the transverse electric-field at 20 kHz.

process. The SNM is a very simple, high-yielding process that reduces manufacturing costs.

2.2. EO measurements

We measured the EO sensitivity of DAST crystals to evaluate their performance as the electric-field sensors [6,7,11]. Since the largest EO coefficient in DAST crystals is r_{11}, the EO effect is expected to be largest along the dielectric principal x-axis, which is almost parallel to the crystallographic a-axis [12]. The DAST crystals are usually planar with (0 0 1) plane as a largest facet and they are expected to be used in transverse electric-field sensors. The authors previously used DAST crystals with different thickness for EO measurement. In addition, we prepared a commercial KTP crystal as a standard EO crystal, which is presently the most attractive crystal ($r_{33} = 36.3 \pm 1.8$ pm/V) among the inorganic materials used in transverse electric-field sensors [13]. Fig. 3 schematically illustrated the EO measurement of the transverse electric-field. The detail of this setup was reported by [7]. Fig. 4 shows the recent results of EO sensitivities measured for the crystals obtained by the SNM as a function of their thickness. The EO sensitivity of DAST crystals was almost proportional to

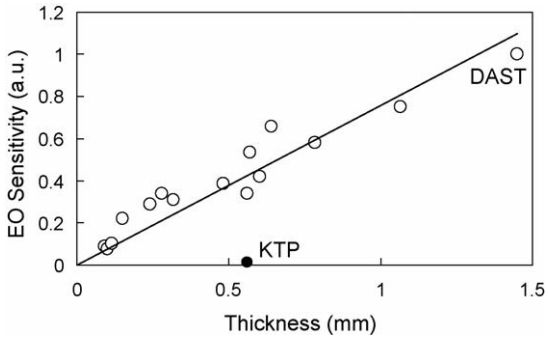

Fig. 4. The dependence of EO sensitivity on the crystal thickness.

the thickness of the crystals, which in turn indicates that the qualities of the crystals were almost the same. We also observed the EO sensitivity of DAST crystal exhibited an increase of more than 45-fold that of the KTP crystal with almost same thickness (KTP: 0.56 mm, DAST: 0.57 mm). Thicker DAST crystals tended to show high-sensitivity compared to thinner crystals. From these results, it is evident that DAST crystals, especially thicker crystals, have high-sensitivity compared to the reliable KTP crystal for the use of the transverse electric-field sensors.

2.3. THz wave generation

Proposed THz generation systems using DAST crystals include the optical rectification of a femtosecond-laser pulse [14] and coherent THz wave generation using a dual-wavelength oscillating Ti:sapphire laser and an OPO [15,16]. The authors previously demonstrated widely tunable THz wave generation from DAST crystals by DFG using KTP-based OPO in the range of 1064 and 1450 nm [17,18]. Recently, the authors modified the arrangement of the THz generation system. Fig. 5 illustrates the experimental setup for THz wave generation using a DAST crystal. The detail of this setup is reported by [8].

Fig. 6 shows the THz wave peak power obtained from the DAST crystal. In the range of 2–31.5 THz, the DAST crystal generated strong, continuously tunable THz waves. The maximum output energy of the THz wave was 110 nJ/pulse at 18.8 THz. Since the pulse duration of OPO was approximately 8 ns, the peak power of the THz wave was estimated to be 13.4 W at 18.8 THz. However, the THz power decreased at around 22 THz, mainly due to the absorption of the black polyethylene filter. The

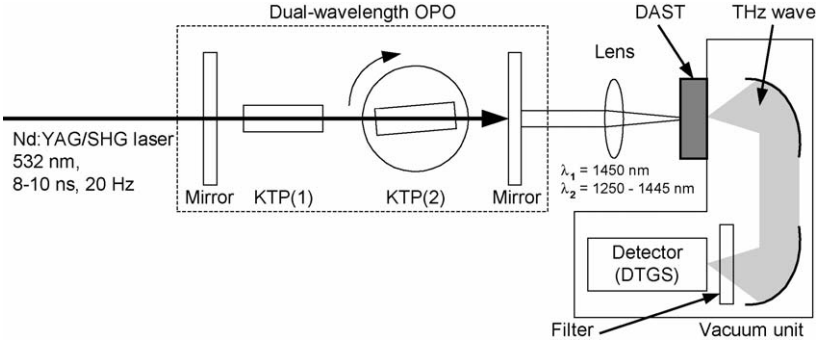

Fig. 5. Setup for THz wave generation using difference frequency mixing based on KTP-OPO.

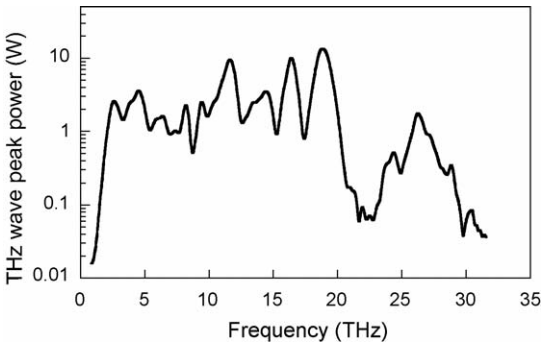

Fig. 6. THz-wave peak power obtained from 1-mm-thick DAST crystal.

other small energy reductions at 8.5, 15, 17.5, 25 and 28 THz would be due to the absorption of the DAST crystals. The infrared and Raman spectroscopy of the DAST crystals indicated active molecular vibrational modes [18]. Although DAST crystals have the above absorption, they are suitable for widely tunable THz wave generation. Subsequently, the authors tested the stability of THz wave generation at 4.5 THz. The energy of the two input laser beams (1450 and 1419 nm wavelengths) was 0.7 mJ. Fig. 7 shows the results of the test. THz power obtained from a DAST crystal was constant during 10 h (Fig. 7(a)). In contrast, THz power obtained from the other DAST crystal suddenly decreased in less than 1 h (Fig. 7(b)) [18]. After the experiments, we observed the laser damage in the crystal which showed the decrease of THz power. Fig. 8 shows the DAST crystal with damage. These results indicate as follows: (1) DAST crystals essentially have high-tolerance of laser irradiation and great potential as a reliable NLO crystal for THz applications. (2) Some DAST crystals have origins of laser damages. About the origins of laser damages, we are investigating at present and would like to report in future.

2.4. Laser-induced nucleation

By introducing SNM, we could grow higher quality DAST crystals than by the conventional growth method. SNM is a useful method for controlling the growth position of sponta-

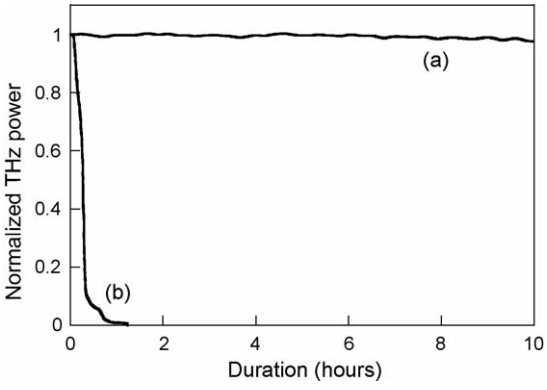

Fig. 7. The results of 10-h stability test of 4.5 THz generation using DAST crystals. (a) THz power was constant during 10 h. (b) THz power suddenly decreased in less than 1 h. THz-wave power was normalized to the initial peak power.

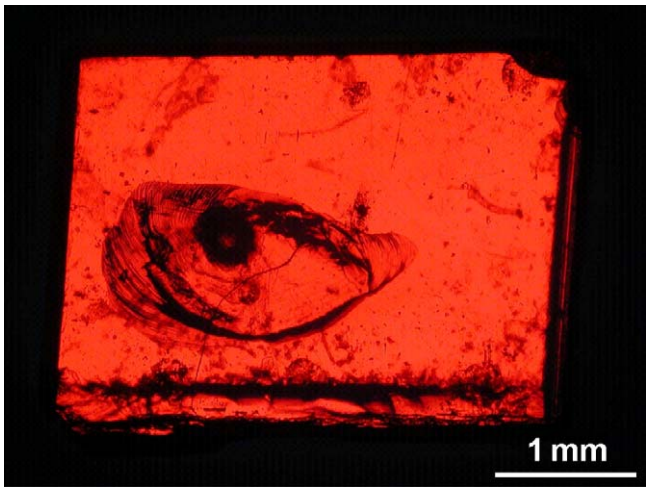

Fig. 8. Photograph of laser damage in a DAST crystal.

neously nucleated DAST crystals. However, it is difficult to control the period of nucleation because DAST solution possesses the large meta-stable region [19]. Normally, in DAST solution, spontaneous nucleation occurs at temperature below the saturation point (i.e., the highly supersaturated region). The nuclei generated spontaneously in a highly supersaturated solution grow rapidly after nucleation, leading to poor crystallinity. Moreover, many crystals generate simultaneously in such a solution, leading to poly crystals and preventing from growing large crystals. If the nuclei can be spontaneously generated in a low-supersaturated solution by triggering nucleation, the crystal would grow slowly and would be expected to have high-crystallinity. Several methods to externally trigger nucleation in organic solution have been also investigated [20–22]. The authors previously investigated the effect of intense short-pulse laser irradiation on DAST crystallization in a supersaturated solution. Effective crystallization was observed when a 1064 nm near-infrared pulse of an intense Nd:YAG laser, with a pulse duration of 23 ns and a repetition rate of 10 Hz, was irradiated into a supersaturated DAST solution [23]. The authors also turned out attention to an intense femtosecond-laser as a more intense trigger and prepared the setup as shown in Fig. 9. Growth

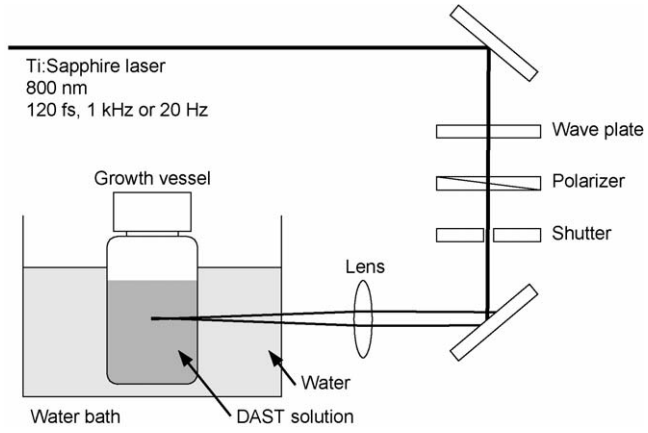

Fig. 9. Setup for femtosecond-laser irradiation into a DAST solution.

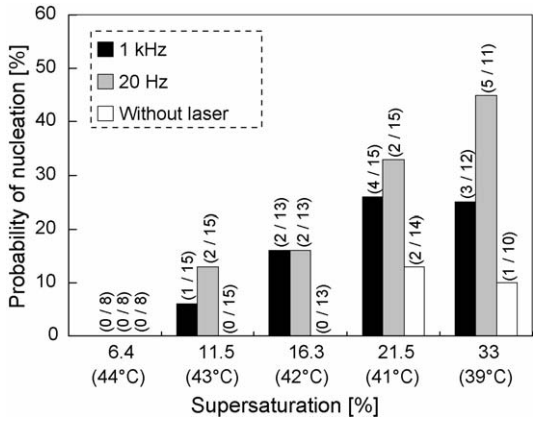

Fig. 10. The probability of nucleation in 24 h after the femtosecond laser irradiation with the repetition rate of 1 kHz (black bar) or 20 Hz (grey bar) and without irradiation (white bar). DAST solutions which had the same concentration (35 g/l), the same quantity (10 ml) and the different supersaturation (6.4–33%) were used. Parentheses in the figure are the number of vessels (α) in which crystals were observed out of the total number of vessels (β), which was indicated as α/β.

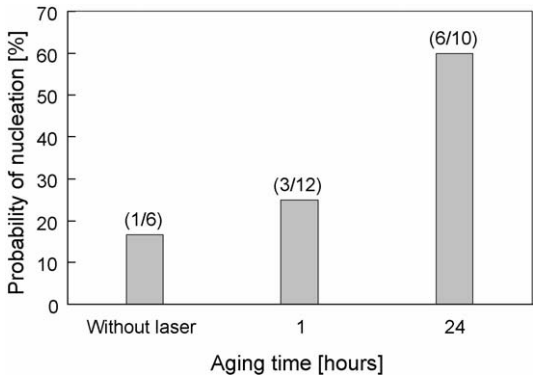

Fig. 11. The dependence of nucleation probability on aging time. Parentheses in the figure are the number of vessels (α) in which crystals were observed out of the total number of vessels (β), which was indicated as α/β.

vessels containing 10 ml DAST solutions (the concentration of 35 g/l, saturation point of 45 °C) were prepared to investigate the effect of laser irradiation. Ti:sapphire laser system (800 nm) was used with pulse duration of 120 fs, a repetition rate of 1 kHz or 20 Hz and pulse energy of 300 μJ. Growth vessels with DAST solution were placed in a water bath to maintain their temperature and investigated the probability of laser-induced nucleation in the supersaturated DAST solution [9]. A laser beam focused by a lens with focal length of 170 mm was irradiated into a supersaturated solution during 30 s. After the irradiation, we continuously observed solutions to check the crystallization during 24 h. Fig. 10 shows the results of nucleation probability in 24 h after laser irradiation. At the all temperature, the probability of nucleation with laser irradiation was more than that without irradiation. Especially, the cases of 42 and 43 °C, which were low-supersaturated and uncrystallized spontaneously, showed that crystallization was observed only in the laser-irradiated solution. These results revealed that femtosecond-laser irradiation could increase the probability of nucleation, especially in the low-supersaturated solution; that is to say, laser irradiation could promote nucleation.

Several years ago, Zaccaro et al. reported the laser-induced nucleation of glycine when they changed the aging time, which was the duration before laser irradiation [24]. Recently, we also investigated the probability of DAST nucleation under different aging time. We used the same experimental setup in shown in Fig. 9. We prepared the DAST solutions (the concentration of 35 g/l, saturation point of 45 °C) and heated them to dissolve the DAST completely. Then the solutions were slowly cooled to 40 °C and held them at that temperature. In this experiment, aging time was the duration from the time solution was cooled to 40 °C until the time before laser irradiation. We changed only the aging time and continuously observed solutions to check the crystallization during 5 days from the beginning of aging time. Fig. 11 shows the experimental results. The left graph shows the probability of nucleation without laser irradiation; the center and the right graphs show that with laser irradiation. The probability of nucleation was enhanced by the increase of aging time; especially more than 50% probability was achieved by 24-h aging.

In order to confirm the influence of laser irradiation on the crystallinity, we also measured the crystallinity of DAST crystals grown from the laser-induced nuclei. The FWHM of DAST (001) XRD rocking curves were conducted on six samples. The FWHM of the DAST crystals grown from laser-induced nuclei were from 20 to 38 arcsec. These values were almost same as the values of crystals grown by SNM previously (from 13 to 33 arcsec, five samples) [6]. These results indicated that aging the solution prior to laser irradiation could enhance the probability of nucleation and laser irradiation had little influence on DAST crystallinity, they mean femtosecond-laser irradiation under the supersaturated solution is effective to promote nucleation. This technique may be used to control the period of nucleation in the low-supersaturated solution and lead to grow high-quality crystals in future.

3. Conclusions

We reviewed the crystal growth, EO and THz properties and laser-induced nucleation of DAST. The SNM was effective to grow high-quality DAST crystals. The EO sensitivity of the DAST crystals was almost proportional to their thickness and exhibited an increase of more than 45-fold that of the KTP crystal. The DFG based on the KTP-OPO generated a coherent, widely tunable THz wave in the range of 2–31.5 THz using DAST crystal. We achieved a constant THz wave energy output during 10 h and high-tolerance of laser irradiation. The femtosecond-laser irradiation into the supersaturated solution could increase the probability of nucleation, especially in the low-supersaturated solution. Aging the solution prior to laser irradiation could also enhance the probability of nucleation. More than 50% probability was achieved by 24-h aging. The FWHM of the DAST crystals grown from laser-irradiated nuclei were almost same as the values of crystals grown by SNM. These results indicated that femtosecond-laser irradiation could promote DAST nucleation in the supersaturated solution and had little influence on DAST crystallinity. EO applications, widely

tunable THz wave source using DAST crystals and laser-induced nucleation are promising for future use.

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