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Growth of Nonlinear Optical DAST Crystals

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Abstract: DAST (4-N,N-dimethylamino-4'-N'-methyl stilbazolium tosylate) is an organic salt with one of the highest nonlinear optical susceptibilities and electro-optical coefficients. DAST crystals are therefore seen as good candidates for many photonic applications such as microring resonators or for THz-devices. The quality of such organic crystal is crucial for any application. We discuss here two different growth methods of single crystalline DAST from solution. Bulk crystals, 1 cm^3 in size, and thin crystals, 1 mm^2 for a thickness of about 100 µm are obtained. The use of a DAST crystal for a microring resonator is also presented

Keywords: DAST · Nonlinear crystal · Organic crystal growth · Rainbow Photonics · Thin film · Terahertz

Introduction

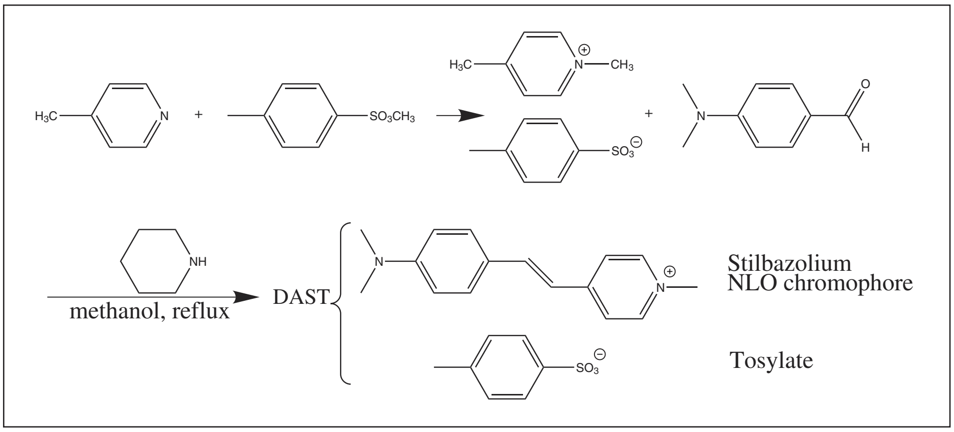
Materials with large nonlinear optical and electro-optical properties are very important for photonic applications [1][2]. If well designed, organic materials may be superior to their inorganic counterparts as the result of the combination of high non-linearities and the almost purely electronic origin of the electro-optical effect, which allows shorter response times.

One of the most promising nonlinear organic salts is 4-N,N-dimethylamino-4'-N'-methyl stilbazolium tosylate (DAST). DAST crystals have a large second-order nonlinear optical coefficient, *e.g.* d_{11}= 1010 ± 110 pm/V at 1318 nm [3], a high electro-optical coefficient, r_{11}= 50 ± 5pm/V at 1313 nm [4], which are respectively 10 times and twice as large as those of the inorganic standard $LiNbO_3$, and a low dielectric constant, ε_{11}=5.2 [4]. Nevertheless, a high crystalline quality is needed for any conceivable application and we concentrate here on the growth of DAST crystal.

Material and Results

DAST is synthesized by the condensation of 4-methyl-N-methyl pyridinium tosylate [5], which was prepared from 4-picoline and methyl toluenesulphonate, and 4-N,N-dimethylamino-benzaldehyde in the presence of piperidine (Scheme). DAST is then purified (>99.8%) by recrystallisation from water and methanol. This orange hydrated form of DAST loses all its water at 140 °C and anhydrous DAST crystals appear as red plates with the monoclinic space group Cc. In this crystal, the stilbazolium, one of the most efficient nonlinear optic chromophores, is the nonlinear optically active part. The anion (tosylate) induces the non-centrosymmetric macroscopic crystal packing.

Since DAST is a two-component organic salt, which decomposes before reaching the melt temperature (256 °C), no growth can be achieved from the melt.



Scheme. DAST Synthesis

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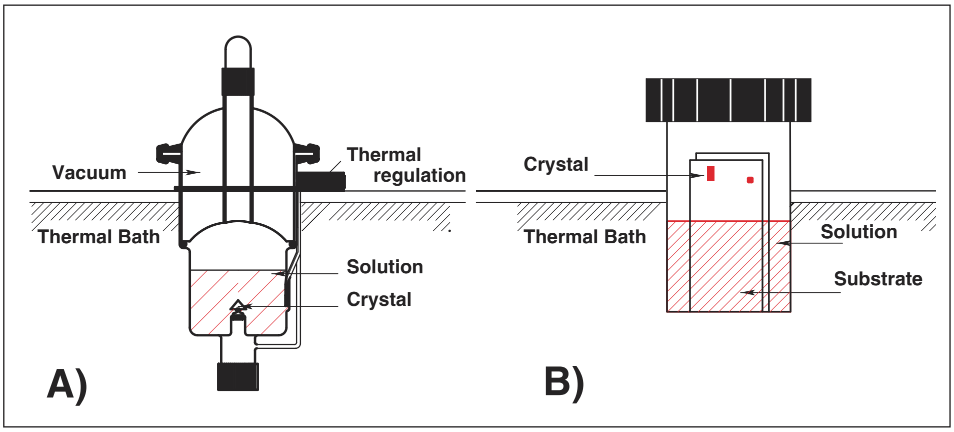

Fig. 1. Schemes of DAST growth methods: A) bulk growth in a seeded saturated solution, B) capillary growth of thin films

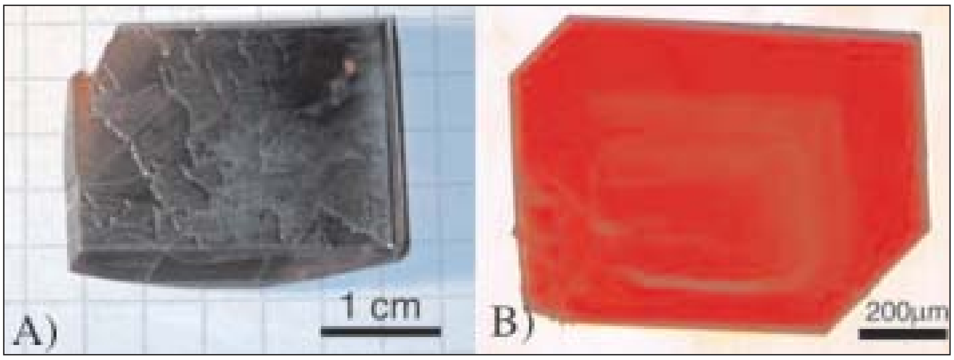

Fig. 2. Two DAST crystals before cutting and polishing. The crystal A) grown in a seeded thermal bath is 0.4 cm thick and the crystal B) grown by capillary method is 80 µm thick.

DAST single crystals are grown from a seeded saturated methanol solution by a controlled temperature lowering technique [5] (Fig 1A). Starting the growth at around 45 °C, the temperature stability of our growth apparatus is within ± 0.002 °C. Since this growth happens at thermal equilibrium, with a slight supersaturation, the growth rate is rather small. Typically a 1 cm^3 crystal is obtained within two months. Therefore the production of bulk crystals requires numerous growth cells working in parallel.

An alternative to the time-consuming bulk growth is the growth of thin films or thin crystals. An effective way is the so-called capillary method shown in Fig. 1B [6]. Two parallel substrates stand vertically in a closed system filled with a DAST-methanol solution. The liquid is pulled up between the substrates by capillarity force. The thermal gradient between the solution and the environmental temperature controls the growth of thin crystals, typically 1 mm^2 for a thickness of 100 µm.

The DAST crystal grows not isotropically but mainly along the (001) crystallographic plane and the polar axis [-100] gives a preferential growth direction (Fig. 2). The cutting and polishing of the bulk crystals is done along the {001} planes and the surfaces are flat to about $\lambda/4$ to $\lambda/2$ (λ = 632.8 nm). One of the main issues of the DAST crystal growth is to prevent the formation of extended defects such as twining or cracks. Indeed, this soft insulator material does not withstand thermal shocks and large thermal gradients can be detrimental for the growth quality. With appropriate conditions, a 10×10×5 mm^3 crystal can be achieved defect-free.

Due to their 2D aspect ratio thin crystals are less sensitive to thermal shock and the thermal gradient can be larger, *i.e.* the growth rate. Therefore extended defects do not usually appear and the crystalline quality is better. On the other hand, this kind of growth is based on spontaneous nucleation and the growth is not well controlled. In addition DAST crystals starting from a spontaneously grown germ seems to have a lower density and the optical quality is lower.

Applications

The importance of optical technologies is expected to increase strongly within the next few years and optical devices should replace pure electronic ones [7]. The rising demand for faster data rates in optical telecommunication networks is pushing high-speed modulation and switching of optical signals. Second-order nonlinear optical materials are therefore very promising. As an example, DAST crystals can be used in integrated high-speed electro-optic modulators such as a set of microring resonators allowing modulator/demodulator functions and fast switching. Straight waveguides form the in-and-output ports and due to evanescent-field-coupling, the waveguides interact with the microresonator, on the top of which an electro-optic material, a DAST crystal, is arranged as shown in Fig. 3.

In the production of such a highly integrated device, the cost of the DAST crystal is a very important criterion. The use of DAST crystals for the generation of THz waves by all solid-state components, a new frequency band between the infrared and the microwaves is also of great interest [8]. Besides high-speed telecommunication, THz pulses can be used to investigate organic and inorganic materials, *e.g.* quality or packing control and tomography. Recently it has been shown that DAST is a good THz emitter using sub-100 fs optical pulses [9].

Conclusion

DAST is a material with very interesting electro-optic properties which could be applied either in optical high-speed telecommunication or in the THz range. The growth of DAST single crystals is crucial and should meet high quality and low price criteria. Whereas the bulk growth produces crystals with a low defect density and a high optical quality, thin films seem to be much cheaper. Improvements in both growth methods should offer a good compromise.

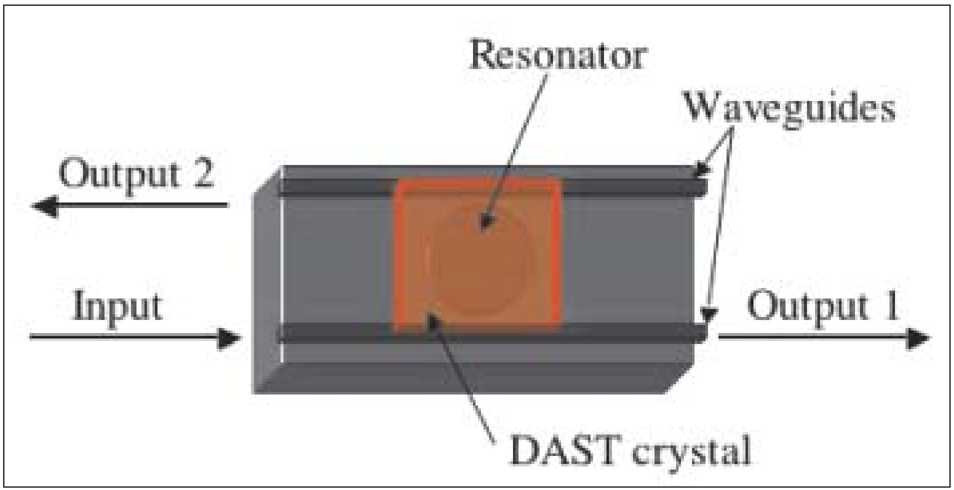

Fig. 3. Scheme of a possible application of DAST: the microring resonator for optical switching

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