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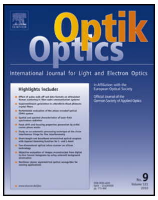

Influence of organic dopants on the optical properties of 4-N,N'-dimethylamino-N'-methyl stilbazolium tosylate crystals

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ABSTRACT

Organic crystals of 4-N,N'-dimethylamino-N'-methyl stilbazolium tosylate (DAST), 2-amino-5-nitro pyridinium (2A5NP) and 2-amino-5-nitro pyridine toluene sulfonate (2A5NPTS) doped DAST crystals were grown by slow cooling method. The powder samples were examined by X-ray diffraction to estimate the lattice parameter values of the crystals. Fourier Transform Infra-Red (FT-IR) and Fourier Transform-Raman (FT-Raman) spectroscopic studies were performed to identify the various functional groups associated with the crystals. The four strong vibrational modes were observed at 1161 cm^{-1}, 1181 cm^{-1}, 1346 cm^{-1} and 1577 cm^{-1} contributing to linear electro-optic effect in DAST crystals. The Density Functional Theory (DFT) was used for FT-IR and FT-Raman analysis by means of the hybrid functional DFT/B3LYP with 6-311 G (d, p) basis set. The optical band-gaps were calculated from the UV–vis and photoluminescence spectra of pure and doped DAST samples.

1. Introduction

The research on organic nonlinear optical (NLO) materials with large NLO co-efficient is strongly motivated by the demand for higher data rates in future optical communication. Due to their almost purely electronic response, they show extremely fast optical nonlinearities of organic counterparts and therefore promise ultrahigh bandwidth photonic devices. Ionic organic materials such as 4-N,N'-dimethylamino-N'-methyl stilbazolium tosylate (DAST) have been used for such optical applications. The materials have the advantages that the alignment of ionic chromophore can be controlled in a polar structure by changing the counter ion [1]. There is nothing to modify the chemical structure of the chromophore itself after having determined the ionic species with large second-order hyper-polarizability. Recently, a series of stilbazolium derivatives has been studied due to their potential use in second harmonic generation (SHG) and electro-optic (EO) modulator [2–6]. One of the stilbazolium derivatives is DAST, which is the most powerful nonlinear optical material which has been demonstrated to have a very large nonlinear optical (NLO) susceptibility and largest electro-optic (EO) co-efficient [7,8]. It belongs to the monoclinic crystal system with the noncentrosymmetric space group Cc and the point group m. It has the following lattice parameters $a = 10.365$ Å, $b = 11.322$ Å, $c = 17.893$ Å, $Z = 4$ and $\beta = 92.24$[3].

2-Amino-5-nitro pyridinium (2A5NP) and 2-amino-5-nitro pyridinium toluene sulfonate (A5NPTS) are taken as dopants since the crystals have comparatively large hyper-polarizability. They have potential chromophores for second-order nonlinearity. The short and multiple hydrogen-bond networks observed in 2A5NP and 2A5NPTS structures provide the crystalline materials with the improved thermal and chemical stability [9].

In the present study, an influence of such dopants on the growth and characteristics of DAST crystals is investigated. Pure and doped DAST crystals are grown by slow cooling method. The grown crystals are characterized by XRD, FT-IR, and FT-Raman with theoretical calculations, UV–vis and photoluminescence spectroscopic analyses.

2. Experiment

2.1. Synthesis and crystal growth of DAST

DAST was synthesized by the condensation of 4-methyl-N-methyl pyridinium tosylate and 4-N-N'-(dimethylamino)

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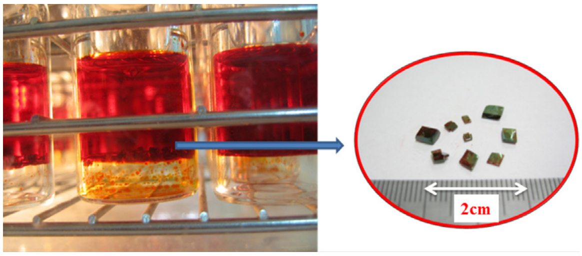

Fig. 1. A clear view of inert fluid-DAST and doped DAST solutions' interfaces.

benzaldehyde in the presence of piperidine [10–12]. 4-Methyl-*N*-methyl pyridinium tosylate used in the condensation reaction was prepared from equimolar quantities of 4-picoline and methyl *p*-toluene sulfonate. The entire synthesis process was conducted in a dry nitrogen atmosphere to avoid the formation of the orange color-hydrated form of DAST material. The synthesized DAST was further purified by recrystallization from methanol. The recrystallized DAST crystals were used for the growth of crystals. 2-amino-5-nitro pyridinium was purchased from Merck (purity >98%). The synthesis of 2-amino-5-nirto pyridinium toluene sulfonate was reported in literature [9].

In our previous report [13], the small-cell experiments were carried out by putting growth cells into a tray and immersing the tray in a constant temperature bath (CBT) for collecting the seed crystals of pure and doped DAST as shown in Fig. 1. A volume of 200 ml DAST solution was saturated at 42 °C and then the solution was filtered. The solution was maintained at equilibrium temperature for 24 h. At the same time, a required amount of 2A5NP and 2A5NPTS was separately added and dissolved into other two respective 200 ml of saturated DAST solutions. The pure, 2A5NP and 2A5NPTS doped DAST solutions were maintained at equilibrium saturation for 24 h. Then, the seed crystals of equal size collected from the small cell experiments were suspended in the respective growth solutions with help of Teflon rods to initiate the growth. A cooling rate of 0.5 °C/day was employed for the growth of the crystals. After 20 days, the grown crystals were carefully harvested.

2.2. Characterization

In order to collect the powder X-ray diffraction data, finely crushed polycrystalline powder of pure and doped DAST crystals were subjected to intense X-rays of Cu*K*α radiation using X-pert PRO PANalytical powder diffractometer. The scan angle was varied from 10° to 80° at a scan rate of 1°/min. The FT-IR spectra of pure and doped DAST samples were recorded in the range of 400–4000 cm^{-1} at a resolution of 1.0 cm^{-1} using a Perkin-Elmer spectrometer by KBr pellet technique. The Raman spectra were recorded using Fourier Transform Raman spectrometer (BRUKER RFS-27) in the range of 50–4000 cm^{-1} at a resolution of 2 cm^{-1}. The absorption spectra of pure and doped DAST samples were studied in the range between 190 and 1100 nm at bandwidth of 0.5–4 nm by Lambda 35 spectrometer. The photoluminescence spectra were recorded in the wavelength from 470 to 800 nm at bandwidth of 5 nm using JASCO fluorescence (FP-8300) spectrometer. The theoretical FT-IR and FT-Raman spectral analyses were carried by means of the hybrid functional DFT/B3LYP with the 6-311 G (d, p) basis set and the time dependent DFT/B3LYP 6-311 G (d, p) was used to compute the theoretical UV–vis spectra in the solvent of methanol available in Gaussian 09 Program [14–16].

3. Results and discussion

3.1. Crystal growth

The grown pure, 2A5NP and 2A5NPTS doped DAST crystals are shown in Fig. 2(a)–(c). The (0 0 1) habit faces grow predominantly and also the growth is observed to be faster in both positive and negative *a* and *b* axes. In the grown crystals, the large (0 0 1) face is found and it is bounded by (1 1 0), (1 −1 0) and small (0 2 0) faces [17]. In case of 2A5NP doped DAST crystals, the growth rate along the *a*-axis is much larger than that of pure crystal. In the 2A5NPTS doped DAST crystals, growth rate along *a* and *b* axes decrease whereas the growth rate along the *c*-axis is found to be high. The different morphologies of pure, 2A5NP and 2A5NPTS doped DAST crystals are shown in Fig. 3(a)–(c).

The variation in the growth rate leads to irregular stacking of the chromophores and tosylates leading to the surface defects like hillocks that are observed in the grown crystals. Normally, the sheets of cationic chromophores are interleaved with sheets of *p*-toluene sulfonate (tosylate) anions along the crystallographic *c*-axis [18]. Also, at high growth rates, the two-dimensional nucleation at corners predominates and there is several two-dimensional nuclei existed simultaneously where new layers nucleated before the lateral growth of the previous layer are completed and hence the hillocks are developed on the former (0 0 1) face. The microscopic image (Fig. 3(d)) shows the orientated rectangular hillocks observed on (0 0 1) face of the DAST crystal. In the case of 2A5NPTS doped DAST crystals, large area faces around the (0 0 1) are developed by too much adhesion of material leading to a rise in supersaturation surrounding them, which in turn causes an increased rate of two-dimensional nucleation and solution inclusion. Since the growth rate along the (0 0 1) direction is very high, 2A5NPTS doped DAST crystal (Fig. 2(c)) exhibit a different morphology as compared to the regular morphology of pure DAST crystals.

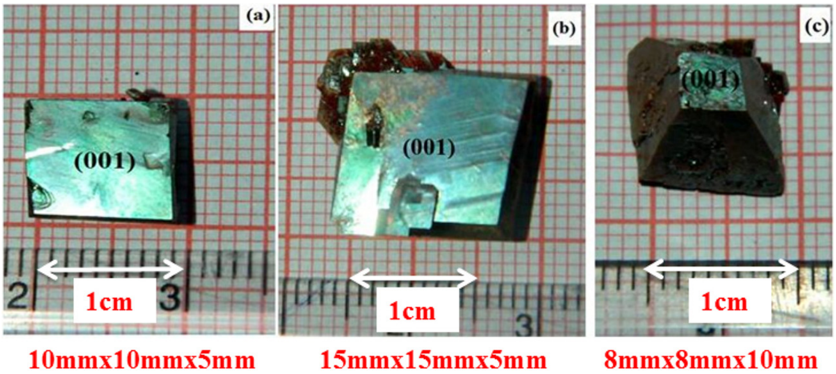

Fig. 2. (a)–(c) Photograph of the grown (a) DAST, (b) 2A5NP doped DAST and (c) 2A5NPTS doped DAST crystals.