Optical Materials 55 (2016) 153–159

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Growth and characterization studies of an efficient semiorganic NLO single crystal: 2-Amino 5-nitropyridinium sulfamate (2A5NPS) by assembled temperature reduction (ATR) method

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ARTICLE INFO

Article history:
Received 12 January 2016
Received in revised form 10 March 2016
Accepted 14 March 2016
Available online 24 March 2016

Keywords:
2-Amino-5-nitropyridine
Semi organic
Orthorhombic
TG/DTA
SONLO
Optical constants

ABSTRACT

Semiorganic crystals of 2-amino 5-nitropyridinium sulfamate (2A5NPS) were grown by slow evaporation and slow cooling method. A asymmetric grown crystal was subjected to single crystal X-ray diffraction and X-ray powder diffraction by using Bruker Kappa APEX11 CCD diffractometer and Philips analytical powder X-ray diffractometer respectively. Vibrational frequency of 1:1 equimolar ratio single crystals of 2-amino 5-nitropyridinium sulfamate (2A5NPS) was measured using FTIR and thermal stability of the grown crystal of 2-amino 5-nitropyridinium sulfamate (2A5NPS) was also measured. Optical properties of the grown crystal and NLO test were also carried out.

1. Introduction

Nonlinear optical materials exhibit prominent characteristics in terms of the fast and parallel processing of a signal, which are required for the applications of optical communication [1,2]. Materials with large nonlinear optical coefficients and wide transparency range have been investigated for a few decades. Among them, organic materials exhibit large nonlinear coefficients, and some physical and chemical factors for the molecular hyperpolarizability are fairly understood [3,4]. A common and often productive route to such materials has been to utilize molecules with electron donating and accepting moieties attached to a conjugated system. The optical response of an SHG active material is influenced by both the chemical purity and structural composition of the bulk sample [5]. On the microscopic level, the efficiency of nonlinear optical effect depends on the molecular polarizability. Up to now, two types of molecule, i.e., dipolar and octopolar molecules, have been studied intensively to enhance their quadratic polarizability [6,7]. Although octupolar molecules can exhibit large hyperpolarizability, dipolar molecules are often chosen as a motif of the nonlinear optical material because it is easy to obtain a bulk crystal. In the case of dipolar molecules, the hyperpolarizability β_{ijk} can be enhanced by adding donor and acceptor groups to a π-electron system in the para position of an aromatic ring. A variety of both organic and inorganic nonlinear crystals have been proposed in the past fifteen years some of them having even reached the level of development and industrialization [8–10]. Inorganics are highly resistant owing to their ionic or covalent nature of their intermolecular bonding, while their figure of merit reaches a plateau exemplified by KTP [11] which may well be a ceiling. In contrast while organic materials are often more fragile their nonlinearity may surpass by several orders of magnitude than that of inorganic materials owing to the possible involvement of highly polarizable π-electron system. Moreover, the structural flexibility of organic molecules and the possibility of precise and adequate organic syntheses assisted by predictive molecular engineering rules may well be a decisive fascinating asset of organics in contrast to the more rigid nature of minerals [12]. The thermal and mechanical stabilities of these organic crystals are not convenient for industrial applications as a frequency doubler of high mean power. In order to improve on these drawbacks, a new type of hybrid organic-inorganic crystal was proposed in 1991 [13]. This crystal engineering provides salts with large nonlinear responses and enhanced stabilities compared to the corresponding molecular organic crystals. Moreover, they exhibit a wider transparency range and bulky crystal morphologies [14,15]. Another important advantage of these organic-inorganic materials is to offer the opportunity of

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http://dx.doi.org/10.1016/j.optmat.2016.03.022
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solid solution existences due to the mineral subnetworks ($H_2PO^{4-}, H_2ASO_4^-, SO_4^{2-}, Br^-, Cl^-$, etc.). Indeed, a gradual evolution of the chemical composition in a solid solution allows to adjust several linear and nonlinear optical parameters as optical indexes, phase matching directions, and optimization of the d_{ij} susceptibility coefficients and to carry out waveguide devices from crystal growth epitaxy [16]. The cohesion of ionic mineral lattices is combined with the enhanced polarizability and flexibility of organic molecules. The noncentrosymmetric packing of ion inorganic crystals of molecules in organic ones is the major challenge in the design of crystalline materials exhibiting ferroic properties and (or) second order optical nonlinearities. Organic crystals built up from molecules containing delocalized π-electron systems asymmetrized by interacting donor and acceptor groups show significant advantages as compared to inorganics, namely, the π-electron rings or chains are highly polarizable [17–19]. The evaluation of molecular second order hyperpolarizability tensor of individual molecules be the EFISH experiment [20–23] is an invaluable asset towards further molecular and crystalline engineering studies. The enhancement of the molecular hyperpolarizability β and of the macroscopic second order susceptibility coefficients χ^2 strongly depends on a variety of all possible chemical modifications [17–19]. This type of material is composed of organic and inorganic ions. These organic-inorganic crystals are tried to combine the advantages of both organic and inorganic compounds: to have convenient mechanical and thermal stabilities through the inorganic sub network and to exhibit large nonlinear optical efficiencies due to the grafted organic molecules. Because of the large hyperpolarizability and the protonation ability in acid solution ($pH < 2$), the molecule of 2-amino 5-nitropyridine (2A5NP) was chosen as the organic part [24]. 2-Amino 5-nitropyridine (2A5NP) is an outstanding chromophore and nonlinear optical material. 2-Amino 5-nitropyridine (2A5NP) is an organic chromophore known for its second-order nonlinear optical properties due to its high hyperpolarizability (27.0×10^{-30} esu) [25]. The protonated cation of this organic base can form compounds with several types of anions, and in some cases, materials exhibiting second harmonic generation (SHG). The association of 2A5NP with some specific anions has resulted in compounds with improved chemical and thermal stability and mechanical resistances, which are important factors to consider for the design of the nonlinear optical materials [15,26]. A remarkable structural property was observed in many of the crystal structures of these materials arrangement of $2A5NP^+$ cation in herringbone motifs connected to anionic layers. Masse et al. have published a series of organic–inorganic crystals of 2A5NP and inorganic acids such as arsenic acid designed for NLO materials. 2A5NP allows for the growth of numerous salt, such as 2-amino 5-nitropyridinium dihydrogen phosphate, 2-amino 5-nitropyridinium arsenate, 2-amino 5-nitropyridinium aceto phosphate, 2-amino 5-nitropyridinium chloride, 2-amino 5-nitropyridinium bromide, 2-amino 5-nitropyridinium -L- monohydrogenate, 2-amino 5-nitropyridinium tetrafluoroborate, 2-amino 5-nitropyridinium selanate, 2-amino 5-nitropyridinium tetraoxcidorhenate (VII) monohydrate. Using an outstanding chromophore and nonlinear optical material, the new structure of 2-amino 5-nitropyridinium hydrogen oxlate (2A5NPHO) was grown and solved. The mechanical and electrical properties of 2-amino 5-nitropyridinium hydrogen oxalate were reported [27,28]. The efficient semi organic crystal of 2-amino 5-nitropyridinium dihydrogen phosphate (2A5NPDP) was grown by using sankaranarayanan-ramasamy (S-R) method and optical, electrical, mechanical and NLO properties were reported [29,30]. The grown crystal of 2-amino 5-nitropyridinium sulfamate (2A5NPS) structure was solved and reported [31]. In this article, we report the synthesis and growth of 2-amino 5-nitropyridinium sulfamate (2A5NPS) by slow cooling method. The as grown 2-amino 5-nitropyridinium sulfamate (2A5NPS) was subjected to XRD, XPRD, FTIR, UV–Vis NIR, NLO and TG/DTA are reported.

2. Material synthesis

The commercially available 2-amino 5-nitropyridine (sigma Alrich > 98%) is a weak bronested and necessary raw material for preparing azo-compounds. 2-Amino 5-nitropyridine has a interesting molecular structure, which has a nitro group as an electron donor and amino group as an electron acceptor. Further, the pyridine ring acts as cationic bonding site, the nitro group as a hydrogen acceptor and the amino group as a hydrogen donor. The 1:1 organic-inorganic 2-amino 5-nitropyridine sulfamate was obtained at room temperature in distilled water. The chemical structure is illustrated in Figs. 1 and 2.

3. Crystal growth

The bulk crystal of 2-amino 5-nitropyridinium sulfamate (2A5NPS) was grown by slow cooling method using assembled temperature reduction apparatus (ATR) as shown in Fig. 4. A pure seed crystal that was grown by slow evaporation was mounted on the crystal holder. The crystal holder is made up of acrylic used to stirrer the saturated solution very well and makes the solution more stable. The crystal holder was connected to microcontroller, which is used to rotate crystallizer clock and anticlockwise. From this bidirectional rotation, inhomogeneous and inclusions in the crystal will be avoided. The crystal was grown in 500 ml standard crystallizer. The saturated solution was filtered using Whatman filter paper. The crystallizer was controlled by using external water bath whose temperature fluctuation is less than 0.01 °C. The temperature of the saturated solution was 40 °C. Then the saturated solution was over heated up to 50 °C of one day. Then the temperature was reduced by 2 °C/h, higher than the saturation point and again the temperature was decreased to saturated point 1 °C/day. $5 \times 3 \times 2$ mm^3 pure 2-amino 5-nitropyridinium sulfamate (2A5NPS) crystal was fixed at centre of crystal holder. From the saturated point, the temperature was decreased at the rate of 0.5 °C/day. A bulk crystal of 2-amino 5-nitropyridinium sulfamate (2A5NPS) was harvested after 60 days. The size of the crystal is $25 \times 20 \times 20$ mm^3. The grown crystal and growth apparatus are shown in Figs. 3 and 4 respectively.

4. Results and discussion

4.1. Single crystal X-ray diffraction

The single crystal X-ray diffraction was measured by Brucker Kappa Apex11 CCD diffractometer with Mo Kα radiation $\lambda = 0.71073$ Å was employed to collect the single X-ray diffraction data of 2-amino 5-nitropyridinium sulfamate (2A5NPS). The single

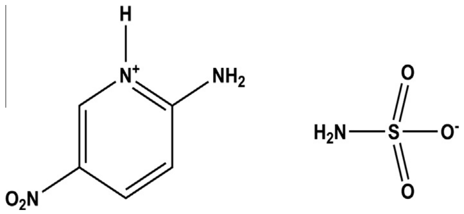

Fig. 1. Structure of 2-amino 5-nitropyridinium sulfamate (2A5NPS).