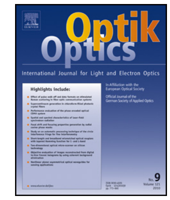
Optik 124 (2013) 5898–5905

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo



Growth and characterization of pure and doped organic nonlinear optical single crystal: L-Alanine alaninium nitrate (LAAN)

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ARTICLE INFO

Article history:
Received 19 November 2012
Accepted 16 April 2013

Keywords:
Nonlinear optics
Organic materials
Doping effects
X-ray diffraction
Electrical measurements

ABSTRACT

The pure L-alanine alaninium nitrate (LAAN) single crystals and LAAN crystals doped with lanthanum oxide (La_2O_3), sodium chloride (NaCl), urea (CH_4N_2O), glycine ($C_2H_5NO_2$) and thiourea (CH_4N_2S) were grown by slow evaporation method. The X-ray diffraction analysis, scanning electron microscopy (SEM), energy dispersive X-ray (EDAX) analysis, UV–vis spectral analysis, dielectric studies and powder SHG measurement are studied systematically. The slight changes in the lattice parameters were observed for the doped crystals compared to pure LAAN crystal. The incorporation of doping into the crystal lattice was confirmed by energy dispersive X-ray analysis. There is no change in the transmission window due to doping and the percentage of transmission in doped samples was found to increase as compared to that of pure LAAN crystal. The dielectric constant of pure crystal was found to be less than that of doped crystals. The AC conductivity was found to increase after doping and with the increase in temperature. A green radiation of 532 nm was observed from the pure and doped LAAN crystals confirming the second harmonic generation (SHG) of the crystals.

1. Introduction

In recent years, nonlinear optical (NLO) materials have attracted considerable attention due to their applications in laser technology, optical communications, optical switching, data storage, optical mixing and electro-optic applications. The development of organic materials suitable for nonlinear optical devices is of interest because of high nonlinearity when compared to that of conventional inorganic materials. A considerable interest has been shown recently in studying the effect of impurities (both inorganic and organic) on the nucleation, growth and physical properties of some hydrogen bonded crystals like potassium dihydrogen phosphate (KDP), ammonium dihydrogen phosphate (ADP), magnesium sulphate heptahydrate (MSH), ammonium oxalate monohydrate (AOM), and zinc tris (thiourea) sulphate (ZTS) [1–9]. The presence of impurity molecules even at lower concentrations in the parent solute may have considerable effect on growth kinetics and other properties. Several interesting results have already been reported on several properties of doped KDP [1–3], AOM [4,5], MSH [6,7], and ZTS [8,9] crystals. Some reports are also available on doped ADP single crystals [1,10]. Ananda Kumari and Chandramani [11] have found that the KDP crystals containing alkali halides such as potassium chloride (KCl)/sodium chloride (NaCl)/potassium bromide (KBr)/sodium bromide (NaBr)/potassium iodide (KI)/sodium iodide (NaI) shows appreciable increase in second harmonic generation (SHG) efficiency compared to pure KDP crystals. Deepa et al. [12], have showed that the alkali halide (NaCl/NaBr) addition reduces the DC conductivity of KDP single crystals. Anne Assencia and Mahadevan [10] have observed the DC conductivity of ADP single crystal increases with the increase in impurity (urea/thiourea) concentration. Mahadevan [13] has found that the DC conductivity does not vary systematically with impurity concentration in the case of KCl added MSH single crystals. However, the conductivity is larger for impurity added crystals than the pure crystals. Meena and Mahadevan [1] have reported that L-arginine ($C_6H_{14}N_4O_2$) addition leads to reduction of electrical parameters of KDP and ADP single crystals. Considering the above, it can be understood that impurity (various types) addition to L-alanine alaninium nitrate (LAAN) is expected to make it a more interesting material. Therefore understanding the effect of different kinds of impurities on the physical properties of this material needs more investigations. The L-alanine alaninium nitrate (LAAN) belongs to the family of organic nonlinear optical material and grown from its aqueous solution by slow evaporation technique at room temperature. The characterizations of the grown single crystals were investigated by many researchers [14–19]. The L-alanine alaninium nitrate (LAAN) was first crystallized by Manuela Ramos Silva [20], which belongs to the monoclinic crystal system with space group $P2_1$ with cell parameters $a = 7.8578\,(5)$ Å, $b = 5.4516\,(6)$ Å, $c = 12.8276\,(7)$ Å and $\beta = 94.73\,(4)^\circ$. In our present

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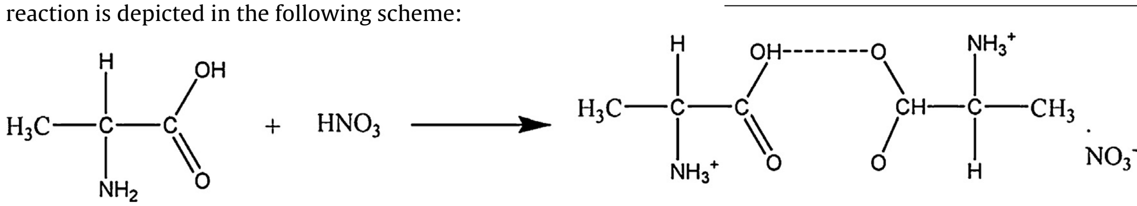
0030-4026/$ – see front matter © 2013 Elsevier GmbH. All rights reserved.
http://dx.doi.org/10.1016/j.ijleo.2013.04.047

work, L-alanine ($C_3H_7NO_2$) mixed with nitric acid (HNO_3) (2:1) was grown from an aqueous solution by the solvent evaporation technique. We have investigated for the first time the effect of lanthanum oxide (La_2O_3), sodium chloride (NaCl), urea (CH_4N_2O), glycine ($C_2H_5NO_2$) and thiourea (CH_4N_2S) as impurities on the properties of LAAN and results obtained are reported and discussed in this paper.

2. Experimental procedure

2.1. Synthesis of pure and doped LAAN

The single crystal of LAAN was synthesized from L-alanine and nitric acid taken in the stoichiometric ratio of 2:1. The chemical reaction is depicted in the following scheme:



The calculated amounts of L-alanine and nitric acid were dissolved in double distilled water. In order to synthesize the doped LAAN with (lanthanum oxide, sodium chloride, urea, glycine and thiourea), 6 mol% of these additives were added to the solution of LAAN separately. The solutions of pure and doped LAAN were prepared separately and stirred well using a magnetic stirrer for about 2 h. The solutions were heated at 50 °C until the synthesized salts of pure and doped LAAN were obtained.

2.2. Determination of solubility

It is desirable to study the solubility of the material in a suitable solvent before proceeding for the crystal growth. Solubility must be moderate and should have positive temperature gradient in a selected solvent. Solubility of the pure and doped LAAN in double distilled water was studied gravimetrically at different temperature (30, 40, 50, 60 and 70 °C) [21]. The solutions of pure and doped LAAN were prepared separately and kept at constant temperature for two hours with constant stirring. The homogeneous solutions were kept in the container for an hour without any disturbance. A 10 ml saturated solution of each sample was pipetted out, dried in oven and weighed to measure the dissolved solute. The same process was repeated for different temperature range from 30 to 70 °C in steps of 10 °C. The solubility curves of the pure and doped LAAN crystals are shown in Fig. 1. It can be seen that the solubility increases with temperature for pure and doped LAAN, thus the double distilled water was used as a solvent throughout the experiment. The solubility of doped crystals was found to be less than of pure crystal.

2.3. Single crystal growth

The pure and doped LAAN single crystals were grown by dissolving the synthesized salts in appropriate amount in double distilled water and heated at a constant temperature of 50 °C with continuous stirring using magnetic stirrer for two hours to form saturated solutions. The saturated solution of each sample is then filtered using filter papers. The filtered solutions were kept in borosil beakers covered with porous thin plastic sheet and allowed to crystallize by slow evaporation of the solvent at room temperature. The colorless crystals of pure LAAN (1.7 cm × 1.3 cm), La_2O_3 doped LAAN (~3.0 cm × 2.2 cm), NaCl doped LAAN (~1.3 cm × 0.8 cm), urea doped LAAN (~4.6 cm × 1.8 cm), glycine doped LAAN (~2.0 cm × 0.8 cm) and thiourea doped LAAN (~1.9 cm × 0.7 cm) were harvested within three to four weeks as shown in Fig. 2.

3. Results and discussion

3.1. X-ray diffraction studies

Single crystal X-ray diffraction analysis of the pure and doped crystals were carried out using Nonius CAD-4/MACH3 diffractometer with Mo–Kα radiation (λ = 0.71073 Å) to identify the structure and to estimate the lattice parameters. The lattice parameter values recorded from single crystal XRD analysis for the pure and doped LAAN crystals are given in Table 1. This analysis revealed that the pure and doped LAAN crystals belong to monoclinic system with the space group $P2_1$ which is recognized as non centrosymmetric, thus satisfying one of the basic and essential material requirements for the SHG activity of the crystals. The obtained crystallographic data of pure LAAN are in good agreement with the reported values [14,15,18,20]. From Table 1, it can be seen that, there is no change in the (monoclinic) phase structure of the doped samples; however the slight changes in lattice parameters was observed for the doped samples compared to pure LAAN crystal. The presence of dopants in LAAN crystal may produce lattice strain which leads to change in unit cell parameters of the doped samples [21,22].

3.2. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDAX) analysis

The SEM studies give information about surface morphology and also can be used to check the presence of imperfections in the grown crystals. The SEM images of the pure and doped LAAN crystals were recorded using Quanta 200 with Genesis eds software and are shown in Fig. 3. The SEM photos exhibit the effectiveness of the impurity in changing the surface morphology of LAAN crystal.

The energy dispersive X-ray analysis (EDAX) is an important tool for characterizing the elements present in the crystal and to

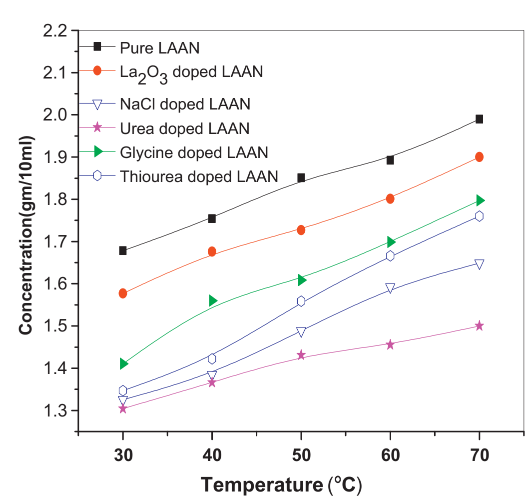


Fig. 1. The solubility diagram of pure and doped LAAN crystals.