Optik 125 (2014) 5515–5518

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo

Studies on the growth aspects and characterization of sodium para-nitro phenolate single crystals for nonlinear optical applications

M. Mahadevan[a,b], P. Anandan[c,d], K. Ramachandran[a,*], M. Arivanandhan[d], Y. Hayakawa[d]

[a] Department of Physics, SRM University, Vadapalani Campus, Chennai 600026, India
[b] Department of Physics, Adhiparasakthi Engineering College, Melmaruvathur 603319, India
[c] Department of Physics, Thiruvalluvar College of Engineering and Technology, Vandavasi 604505, India
[d] Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Naka-Ku, Hamamatsu 432-8011, Japan

ARTICLE INFO

Article history:
Received 3 October 2013
Accepted 1 May 2014

Keywords:
Optical materials
Crystal growth
X-ray diffraction
Thermogravimetric analysis

ABSTRACT

Using slow evaporation solution growth technique, single crystals of sodium para nitro phenolate have been grown from the solutions prepared from three different molecular ratios of para-nitro phenol and sodium hydroxide. Structural analyses were carried out by powder X-ray diffraction and Fourier transform infrared spectrum to conform the grown crystals. Thermal stability of the grown crystals was studied by thermogravimetric (TG) and differential thermal analyses (DTA). UV–vis spectral analysis has been carried out to find the cut off wavelength of the grown crystals. Variations in the cut off wavelengths have been observed. Nonlinear optical property has been confirmed by Kurtz powder technique. The observed optical properties have confirmed that the molar concentration of para nitro phenol influenced significantly on the linear and nonlinear optical properties.

1. Introduction

Various industrial applications of single crystals made the phenomena of crystal growth as one of the thrust areas of research for the past few decades. The crystals are classified in to three categories as organic, inorganic and semi organic single crystals depending upon the raw chemicals used for the growth of single crystals. Since the semi organic single crystals possess the good properties of both organic and inorganic crystals, scientists and researchers focused their interest in growing variety of semi organic single crystals [1–3]. Para nitro phenol was identified as potential organic material which gives variety of derivatives with alkali metal hydroxides [4–10]. Single crystals of potassium para nitrophenolate dihydrate have been grown and some new bonding properties have been reported by Boaz et al. [4]. Lithium para nitrophenolate trihydrate crystal has been reported by same authors and studied the properties to some extent [5]. The same crystal has also been grown by recently developed SR method and some properties have been reported [6]. Sodium para nitrophenolate (NPNa) has different hydrated form when it is grown from water solvent. The dihydrate form of NPNa has NLO activity, but tetrahydrate does not have [11]. Though extensive investigations were carried out on this material [11–15], we are still interested in studying the growth aspects and effect of molar concentration of para nitro phenol of NPNa single crystals in different type of solutions prepared with different molar concentrations of para nitro phenol in sodium hydroxide base.

In the present study, single crystals have been grown from three different solutions prepared by changing the molar concentration of para nitro phenol with fixed amount of sodium hydroxide using slow evaporation method. The structural, thermal and optical properties have been studied by suitable methods and detailed report has been presented in this paper.

2. Experimental

2.1. Growth of single crystals

As purchased para nitro phenol (98% pure) and sodium hydroxide (Merk Product) were used as starting materials to prepare the solutions to grow the single crystals of NPNa. Para nitro phenol and sodium hydroxide have been added in 0.25:1, 0.5:1 and 1:1 in excess of double distilled deionized water to prepare different solutions and stirred well. After the solutions became homogeneous (i.e., after continuous stirring for at least 2 h), the solutions were filtered to avoid the inclusion of impurities during the stirring and maintained at room temperature by using a constant temperature bath controlled to an accuracy of ±0.01 °C. The excess solvent

* Corresponding author. Tel.: +91 9790834728.
E-mail address: ramach76@yahoo.com (K. Ramachandran).

http://dx.doi.org/10.1016/j.ijleo.2014.06.083
0030-4026/

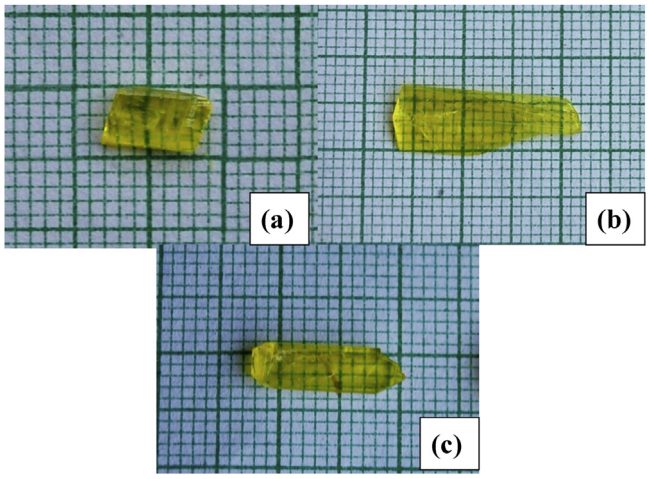

Fig. 1. As grown crystals of (a) 0.25 MNPNa (b) 0.5 MNPNa and (c) 1 MNPNa.

(water) was allowed to evaporate slowly so as to reach the saturation level of the solutions. After the solutions have attained the super saturated level, well controlled evaporation was maintained to avoid the spurious nucleation. Single crystals were grown at room temperature (30 °C) in all the three solutions and the crystals were carefully harvested from the solutions after 20 days. The as grown crystals are shown in Fig. 1. The crystals grown from the solutions prepared from 0.25:1, 0.5:1 and 1:1 molar ratios of para nitro phenol and sodium hydroxide are named as 0.25 MNPNa, 0.5 MNPNa and 1 MNPNa in this study. It is observed that the growth rate of 0.5 MNPNa crystal is greater than that of others.

2.2. Characterization techniques

The grown seed crystals were used to study the properties using various techniques. Powder X-ray diffraction analyses were carried out on the fine crystalline powder sample to conform the crystalline nature of the grown crystal using an X'PERT PRO diffractometer system. The powder samples were mixed separately with KBr 1:20 weight ratio and made as a pellet and the Fourier transform infrared spectra were recorded for the grown crystals by using Perkin Elmer Spectrometer. Linear optical properties of the crystals were studied by UV-Vis Spectrophotometer and nonlinear optical properties were tested by Kurtz–Perry powder technique [16]. Thermo-gravimetric (TG) and differential thermal analysis (DTA) for the crystal samples were carried out in nitrogen atmosphere by a SII Nanotech, EXSTAR TG/DTA 6200 model thermal analyzer to study the thermal properties of the as-grown crystal.

3. Results and discussion

The grown crystals were made as fine powder and subjected to powder X-ray diffraction analyses. The data have been collected at 298 K between 10° and 80° of diffraction angles with the source wave length of 1.5460 Å. The step size of 2θ and the scan step time were fixed as 0.017° and 10.3254 s respectively. The powder X-ray diffraction (PXRD) patterns of all the grown NPNa crystalline powders are shown in Fig. 2. The diffraction pattern contains various reflections corresponding to various crystallographic planes. The sharp peaks of the pattern in all the three samples have been observed which ensures the good quality of crystalline nature of the samples. From the inter-planar distance corresponding to the reflections at different 2θ values along with the intensity and relative intensity of the peaks, it is observed that the grown crystals possess same crystal structure. From this study it is also observed

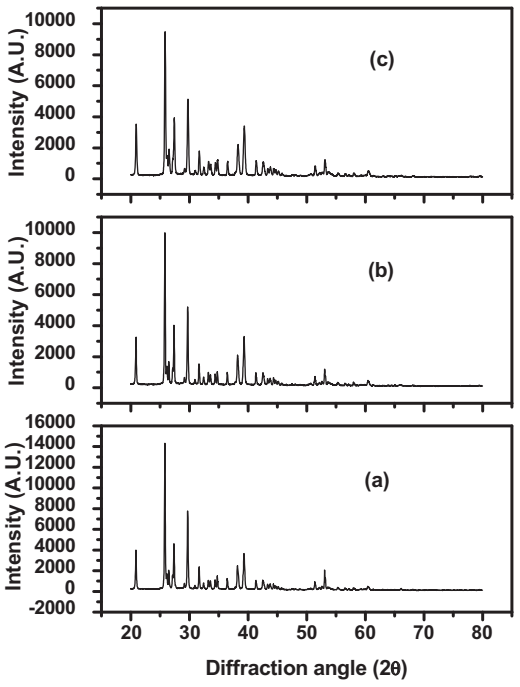

Fig. 2. Powder X-ray diffraction pattern of (a) 0.25 MNPNa (b) 0.5 MNPNa and (c) 1 MNPNa.

that the variation in the molar ratio of para nitro phenol does not alter the crystal structure of the title compound.

For the purpose of analyzing the presence of various functional groups in the grown NPNa crystals the Fourier transform infrared spectra have been recorded in the frequency range between 400 and 4000 cm^{-1}. The recorded FTIR spectra are shown in Fig. 3. Because of the presence of various modes of vibrations, the spectra are found to be complex [17]. The symmetric and asymmetric stretching vibrations due to —OH of lattice water have been observed in the high frequency region near 3400 cm^{-1} as an abroad envelop. Generally these modes of vibration have not been resolved clearly which confirms the presence of hydrogen bonded lattice water in the material [18]. The bending vibration of H—OH of water molecule has been observed at 1696 cm^{-1}. The peak near 1114 cm^{-1} is due to C—O stretching vibration mode which is observed in all crystals. The para substitution usually gives its vibration around 850 cm^{-1} is observed at 858 cm^{-1} in all the spectra. The para substitution NO_2 gives its symmetric stretching vibration

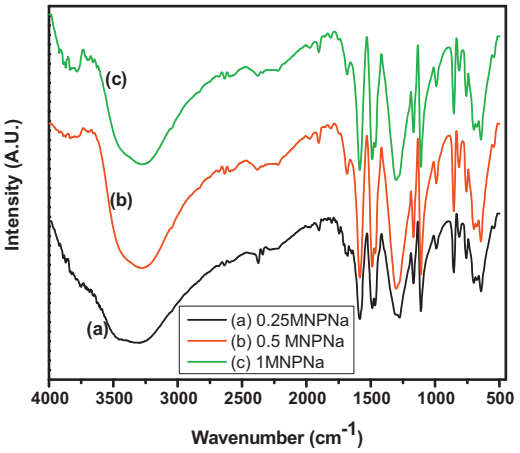

Fig. 3. FTIR spectra of (a) 0.25 MNPNa (b) 0.5 MNPNa and (c) 1 MNPNa.