Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 145 (2015) 329–332

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Effect of solvents on the bulk growth of 4-aminobenzophenone single crystals: A potential material for blue and green lasers

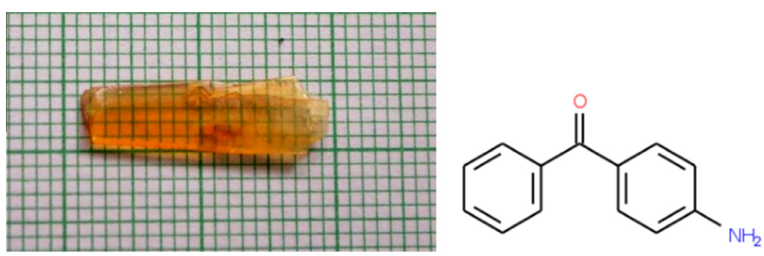
V. Natarajan [a,*], S. Usharani [a], M. Arivanandhan [b,1], P. Anandan [c], Y. Hayakawa [b]

[a] Department of Physics, Dr. Sivanthi Aditanar College of Engineering, Tiruchendur 628215, India
[b] Research Institute of Electronics, Shizuoka University, Johoku 3-5-1, Naka-Ku, Hamamatsu 432-8011, Japan
[c] Department of Physics, Thiruvalluvar College of Engineering and Technology, Vandavasi 604505, India

HIGHLIGHTS

- Effect of solvents on growth aspects of 4-aminobenzophenone was studied.
- The change in enthalpy of 4-ABP was estimated from DTA.
- Highly transparent bulk crystals of 4-ABP were grown from ethanol.
- The transparency of the crystal grown from ethanol was higher than that grown in ethyl acetate.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 October 2014
Received in revised form 23 December 2014
Accepted 2 March 2015
Available online 9 March 2015

Keywords:
Organic compounds
Crystal growth
FTIR spectroscopy
Optical transmission spectroscopy

ABSTRACT

Although 4-aminobenzophenone (4-ABP) is the best derivative of benzophenone with 260 times higher second harmonic generation (SHG) efficiency than potassium dihydrogen phosphate (KDP), growth of high quality bulk crystal still remains a difficult task. In the present work, the effect of solvents on solubility and growth aspects of 4-ABP was investigated to grow inclusion free 4-ABP crystals. The growth processes were discussed based on solute–solvent interaction in two different growth media of ethyl acetate and ethanol. The growth rate and thereby solvent inclusions are relatively higher in ethyl acetate grown crystal than the crystal grown from ethanol. The structural, thermal and optical properties of 4-ABP crystals were studied. The enthalpy of 4-ABP melting process was estimated from differential thermal analysis. The optical transmission study shows that 4-ABP crystals grown from ethanol has high transparency compared to ethyl acetate grown sample due to solvent inclusion in the later crystal.

Introduction

Nonlinear optical (NLO) materials are useful for generating the green and blue lasers by frequency doubling the low frequency laser radiations. Organic NLO crystals are superior to inorganic materials because of their high NLO efficiency and fast response than the inorganic NLO materials [1,2]. Benzophenone and its derivatives are promising organic NLO material with good optical and mechanical properties [3–10]. The derivatives of benzophenone have large NLO susceptibilities and short cut-off wavelengths up to deep UV region (<400 nm) [8–10]. Among the derivatives, 4-aminobenzophenone (4-ABP) is one of the best derivatives of benzophenone with the SHG efficiency of 360 times that of Ammonium dihydrogen Phosphate (ADP) [6,7]. Frazier et al. first reported the growth of 4-ABP in 1987 [10]. The 4-ABP crystal belongs to the monoclinic crystal system. For the growth of 4-ABP, several organic solvents such as ethanol, methanol, dimethyl formamide (DMF) were used as the growth medium in the literature [11]. Despite of huge efforts made by researchers, growth of high quality bulk crystal of 4-ABP still remains as a challenging task. Moreover, it is difficult to grow 4-ABP single crystals

* Corresponding author.
E-mail address: vnatrajan79@gmail.com (V. Natarajan).
[1] *Present address:* Centre for Nanoscience and Technology, Anna University, Chennai 600025, India.

http://dx.doi.org/10.1016/j.saa.2015.03.051
1386-1425/

from solution because it has been readily photo-oxidized [12–14] in solution, which degrades the quality of the resultant crystal [14]. Recently, the 4-ABP single crystals were grown from ethyl acetate and the quality of the crystal was not good as lot of inclusions were found in the crystal [15]. As a consequence, further investigation is needed to grow bulk crystals with less solvent inclusions.

In the present investigation, the solvents' effect on the solute–solvent interaction, solubility and growth aspects of the 4-ABP material were studied to grow inclusion free crystals. The X-ray diffraction (XRD) analysis, thermal analysis and optical transmission studies were performed on the grown crystals to analyze the structural, thermal and optical properties of the 4-ABP.

Solubility and crystal growth of 4-ABP

The 4-ABP materials were purified by recrystallization process using ethanol. In the solution growth process, the solvent can influence on the morphology of the crystal due to its interaction with the surfaces of the growing crystal. Therefore, the selection of suitable solvent for crystal growth is highly imperative in solution growth. Pan et al. [12] investigated the effect of ethanol, methanol and DMF solvents on the growth of 4-ABP crystals. However, the quality of the grown crystals was degraded due to solvent inclusions. In the present investigation, the solubility of 4-ABP in various organic solvents viz., ethyl acetate, ethanol, and o-xylene was measured as a function of temperature. The saturated solution was prepared at a particular temperature and allowed to settle the excess solutes at the bottom of the crystallizer. The saturated solution was collected and the solubility was measured by gravimetric method. The same process was repeated for different temperatures and the solubility curve was obtained. The measured solubility data are shown in Fig. 1 as a function of temperature. The solubility of 4-ABP was increased with temperature in all the solvents. Moreover, the solubility of 4-ABP is relatively high in ethyl acetate whereas it has low solubility in o-xylene.

The saturated solution of 4-ABP was prepared by dissolving the purified source material into the different organic solvents viz. ethyl acetate and ethanol according to the measured solubility data at the temperature of 32 °C. The prepared saturated solutions were homogenized separately by continuous mild stirring of the solutions using a magnetic stirrer by maintaining the temperature of the solution. Then, the saturated solutions were transferred into a crystallizer and covered by a perforated polyethylene sheet for controlled evaporation at room temperature. After the growth period of 4 days, the 4-ABP single crystals were harvested from the crystallizer with ethyl acetate as a solvent. The transparent crystals were obtained from the growth solution of ethanol after a growth period of 21 days. Due to very low solubility of 4-ABP in o-xylene no crystals were obtained in the saturated solution even after 30 days and the solution color was changed from pale yellow to dark pink color possibly due to photo oxidation of the growth solution [14]. Moreover, slight color change was observed in the growth solution of ethanol although it was not affected the quality of the crystal. Whereas, such kind of photo oxidation was not observed in ethyl acetate system due to short growth period. Hence, further observation on the growth aspects has been focused on the other crystals grown in ethyl acetate and ethanol solvents. The photographs of the harvested crystals from ethyl acetate and ethanol with sizes of $28 \times 8 \times 6$ mm^3 and $16 \times 5 \times 4$ mm^3, respectively were shown in Fig. 2a and b.

The structural analysis of the grown crystal was performed by X-ray diffraction analysis using Rigaku X-ray diffractometer. The functional groups of the grown crystal were analyzed by Fourier Transform Infrared (FTIR) spectroscopy. Thermogravimetric and Differential Thermal Analysis (TG and DTA) were performed on the grown crystal to study its thermal properties. Optical transmission characteristics of the grown crystals were studied using double beam UV–Vis-NIR spectrophotometer. Second harmonic generation of the grown crystals was studied by Kurtz–Perry Powder method.

Results and discussion

As can be seen from Fig. 2a, the grown crystal from ethyl acetate has low transparency although the size is relatively larger than the

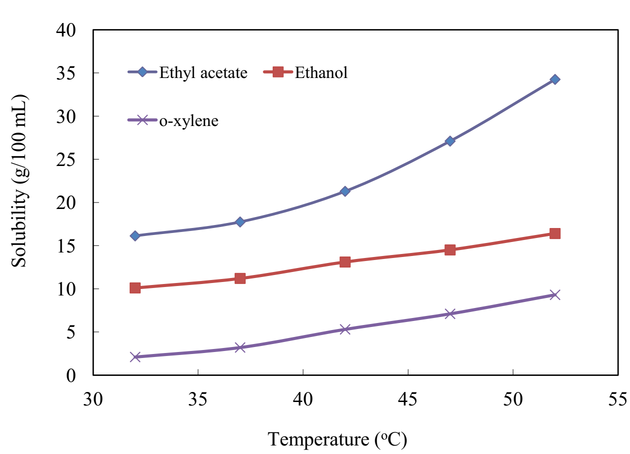


Fig. 1. Solubility curve of 4 ABP in ethyl acetate, ethanol and xylene as function of temperature.

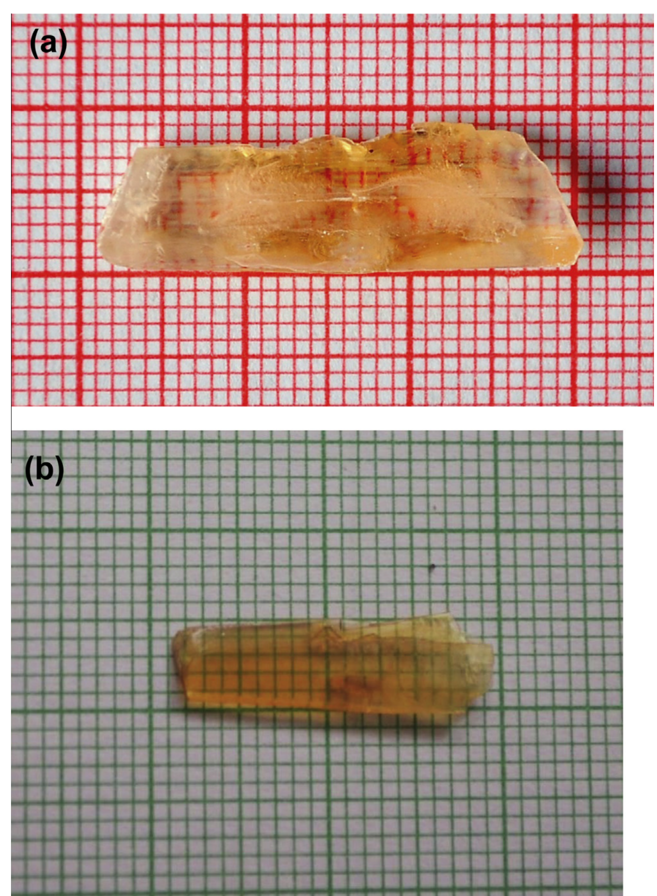


Fig. 2. Photograph of the as-grown crystal of 4-aminobenzophenone under normal ambient condition from (a) ethyl acetate and (b) ethanol.