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Growth and characterization of single crystal of pentachloropyridine

R.N. Rai[a,*], K.B.R. Varma[b]

[a]Department of Chemistry, Birla Institute of Technology and Science, Pilani 333 031, Rajasthan, India
[b]Materials Research Centre, Indian Institute of Science, Bangalore 560 012, India

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Abstract

Bulk single crystals of pentachloropyridine (PCP) were grown by the Bridgman–Stockbarger method. The single crystalline nature of the grown crystals was confirmed using powder X-ray diffraction (XRD) techniques. These were transparent in the 315–2000 nm range. The second harmonic generation (SHG) efficiency of polycrystalline materials using Kurtz powder technique was found to be twice that of the well-known organic nonlinear optical (NLO) material, urea. The mixing behavior of PCP with succinonitrile (SCN) and its effect on SHG and micro-hardness of PCP, along with the physicochemical properties of different compositions of PCP and SCN system were studied in detail. Bulk single crystals of the PCP solid solution containing 0.02 mole fraction of SCN have also been grown using the Bridgman–Stockbarger technique.

Keywords: A1. Crystal growth; A1. Micro-hardness; A1. Optical properties; A1. Second harmonic generation; A1. Temperature profile; A2. Bridgman–-Stockbarger

1. Introduction

The increasing demand on organic materials for technological applications, which includes optical frequency doublers, ultra-fast modulators, amplifiers and switches, has prompted researchers to look for newer promising materials [1–5]. One of the main criteria for an organic nonlinear optical (NLO) material is that its crystal structure lacks a center of symmetry. In molecular crystals, symmetry depends mainly on the polarizability of the electrons in the π-bonding orbital. This is in contrast with inorganic materials where π-electron delocalization is absent and lattice vibrations play a dominant role. Hence, the structural studies related to bonding properties of the atoms in the molecules as well as the molecules in the crystal help in speculating on the properties of material.

*Corresponding author. Tel.: +91 1596 245073 x 276/454; fax: +91 1596 244183.
E-mail address: rn_rai@yahoo.co.in (R.N. Rai).

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The pentachloropyridine (PCP) molecule consists of five atoms of chlorine attached to a pyridine ring containing a nitrogen atom. Therefore, the molecular structure of PCP predicts that it could crystallize in non-centrosymmetric space group. Furthermore, binary organic materials are known to exhibit better optical properties than their parent components [6–8] and, hence, PCP and succinonitrile (SCN) were chosen for the detail study of physicochemical properties and the SHG property.

In this article, we report details concerning the growth of bulk single crystals of PCP and PCP doped with SCN from their melts, along with their micro-hardness, optical and nonlinear optical properties. The comparative properties of PCP crystals to that of PCP doped with SCN, and the phase diagram study of the PCP and SCN system are also reported.

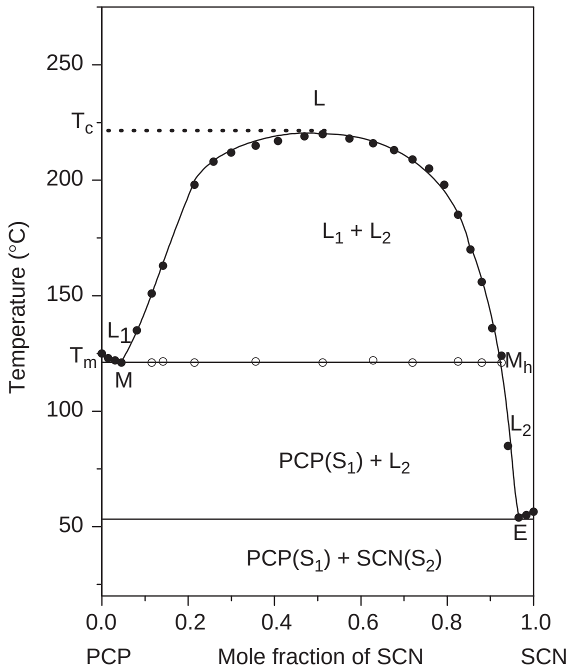

Fig. 1. Phase diagram of pentachloropyridine–succinonitrile system; ●—melting/miscibility temperature.

2. Experimental procedure

2.1. Materials and purification

The purification of SCN (Aldrich, Germany) was done by repeated distillation under reduced pressure, while PCP (Aldrich, Germany) was purified by recrystallization from carbon tetrachloride. The purity of PCP and SCN were checked by their melting points, which were found to be 125 and 56.5 °C, respectively.

2.2. Phase diagram

The phase diagram of the PCP–SCN system was established, using the method reported [9,10], in the form of temperature–composition curve (Fig. 1). The mixtures of two components were taken, covering the entire range of compositions. The melting/miscibility temperatures of each composition were recorded using a melting point apparatus attached with a precision thermometer associated with an accuracy of $\pm 0.5\,°C$.

2.3. Growth of bulk single crystals

To grow the single crystals from their melts, the Bridgman–Stockbarger method was used. Suitable temperature gradients were established in a vertical two zones furnace, having a ceramic baffle that separates the zones, and the temperature of each zone was maintained using two different temperature controllers. The top zone of the furnace was maintained at a higher temperature (130 °C, i.e. 5 °C higher than that of the melting point of PCP) than the bottom zone (110 °C). The optimized temperature profile for growing PCP and PCP doped with SCN crystals is given in Fig. 2. For growing PCP crystals the ampoule-lowering rate was maintained at 4.0 mm/day. When the crystal growth run was completed, the temperature of the furnace was cooled down to room temperature at a rate of 0.5 °C/h.

2.4. Micro-hardness measurement

A Shimadzu Micro Hardness Tester (HMV-2) with a mini load machine and a diamond pyramid indenter was used for the measurement of Vickers hardness and the values were obtained from the following equation, by taking the test load and the