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Investigations on the nucleation studies of sodium paranitrophenolate dihydrate single crystal

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Abstract

Solubility, metastable zonewidth and induction period have been estimated for the growth of sodium paranitrophenolate dihydrate (NPNa) single crystal. The interfacial energy has been calculated using experimentally determined induction period values. Nucleation parameters such as Gibbs free energy, critical energy barrier, radius, number of molecules in the critical nucleus and growth rate have been calculated. The evaluated interfacial tension values are found to be well agreed with the theoretical value derived from the solubility data. Bulk single crystals of NPNa have been grown with an aid of methanol as a solvent by slow evaporation technique.

Keywords: A. Optical materials; B. Crystal growth

1. Introduction

Development of high efficiency non-linear optical (NLO) crystals is of great importance to extend the frequency range provided by normal laser source into the ultraviolet (UV) and infrared (IR) regions [1]. In view of this, it is desirable to search new NLO crystals, possessing shorter cut-off wavelength, high quality, sufficiently large non-linear coefficient, transparency in the ultraviolet region and high damage threshold [2]. The organic NLO crystals have attracted much attention because of the low cost and flexibility as they possess some special properties of large optical non-linearity and low cut-off wavelength in UV region [3]. Although these organic crystals possess favorable optical properties, the mechanical strength of these crystals being low compared to the inorganic counterpart. To overcome this, complex of organic–inorganic gives semiorganic material, which possess higher mechanical strength compared to organic materials. The research on the synthesis of semiorganic materials increased enormously in last few years [4,5]. Sodium paranitrophenolate dihydrate (NPNa) is a potential semiorganic non-linear optical material in which the organic ligand is ionically bonded with the metal ion. Growth and characterization of this material was already discussed in the literature by us [6]. In this paper, the nucleation parameters of NPNa, which are essential for the growth of bulk crystals, have been investigated for the first time. The experimentally determined interfacial tension has been compared with literature reports. Optically good quality bulk single crystals have been grown by slow evaporation technique.

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2. Experimental

2.1. Material synthesis and solubility studies

Sodium paranitrophenolate dihydrate was synthesized by dissolving high purity nitrophenol and sodium hydroxide in the ratio 1:1. The following reaction is expected to take place giving the required compound:

$$NO_2{-}C_6H_4{-}OH + NaOH + H_2O \rightarrow NO_2{-}C_6H_4{-}ONa \cdot 2H_2O \quad (1)$$

The purity of the synthesized salt was improved further by successive re-crystallization process. Solubility studies were carried out using the solvents double-distilled water and methanol. This measurement was performed by dissolving the NPNa salt in double-distilled water and it was kept in constant temperature bath at 303 K. After attaining supersaturation, the equilibrium concentration of the solute was analyzed gravimetrically [7]. The same process was repeated for various temperatures 308–328 K in 5 K interval. The same procedure was repeated for the solution prepared using methanol as solvent. The solubility curve of NPNa is shown in Fig. 1. The solubility increases with increase in temperature for both the solvents. From the graph, it was observed that the solubility of NPNa in methanol is high compared to with that of water.

2.2. Metastable zonewidth and induction period measurements

Saturated solution of NPNa was prepared for the nucleation experiments. The studies were carried out in a constant temperature bath controlled to an accuracy of ±0.1 K, provided with a cryostat for cooling below room temperatures. A constant volume of 50 ml of solution was used in all experiments. The solution was preheated to 5 K above the saturated temperature for homogenization and left at the superheated temperature for 1 h before cooling. The solution was continuously stirred using a motorized stirrer to ensure homogeneous concentration and temperature. Metastable zonewidth of NPNa solution (Fig. 2) was measured by the conventional polythermal method [8]. In polythermal method, the equilibrium-saturated solution is cooled from the overheated temperature and till the temperature at which the first visible crystal nucleus is observed. Since time taken for the formation of first visible nucleus after the attainment of critical nucleus is very small, the first nucleus observed may be taken as critical nucleus.

The saturated solution was preheated at different temperatures (303, 308 and 313 K) for the induction period measurements by isothermal method [9]. Since the time required for the growth of critical nucleus to the detectable size is negligibly small, the time interval between the achievement of supersaturation and the appearance of a crystal of detectable size is measured as induction period. The induction periods were measured for different saturation values. Induction period as a function of supersaturation is shown in Fig. 3.

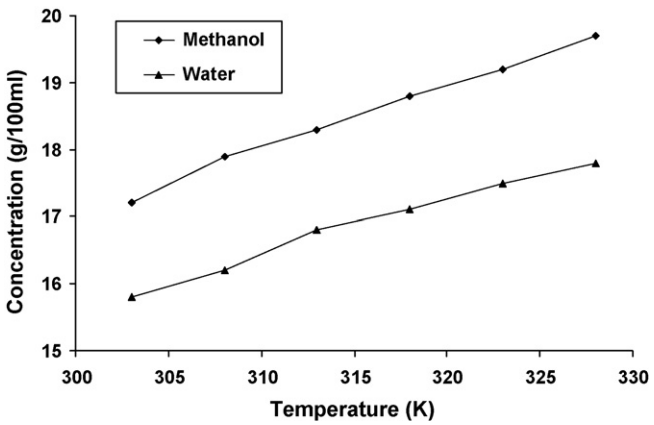

Fig. 1. Solubility of NPNa as a function of temperature.