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Linear and nonlinear optical characterization of methyl-p-hydroxybenzoate (p-MHB) single crystal grown by TSSG method

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ABSTRACT

The nonlinear optical single crystal methyl-p-hydroxybenzoate (p-MHB) was grown by employing top seeded solution growth method (TSSG) for the first time. A good quality small size crystal grown from methanol solution was inserted into the melt as a seed for growth after seasoning it around the melt temperature. Highly transparent optical quality p-MHB single crystal with regular faceting was harvested after the successful growth run. The unit cell parameter of the grown crystal was determined by powder X-ray diffraction (PXRD) and the crystal structure was confirmed by single crystal X-ray diffraction (SCXRD) methods. The UV–Vis–NIR absorption spectrum has been recorded in the range 200–2700 nm and it shows that the lower cutoff wavelength exits at 307 nm. The study indicates that the grown crystal has good optical transparency window in the visible and near IR region in the range 307–2136 nm. Second harmonic generation (SHG) efficiency of the grown crystal was studied by Kurtz-Perry powder method with 1064 nm Nd: YAG laser beam as a fundamental source and it was about twice that the standard KDP.

1. Introduction

In recent years, there were great demands for organic NLO materials as they show very high nonlinear susceptibilities and quick response in selected applications when compared to the conventional inorganic nonlinear optical materials [1]. They are widely used in potential applications such as in the fabrication of electronic and optoelectronic devices, laser technology, optical communication, data storage etc., [2–4]. Kityk et al., reported that large second harmonic generation (SHG) excited by an Nd:YAG laser (λ=1.32 µm) has been observed during the investigation of the optical poling process in 2-(stilbene-4-yl)benzoxazole derivatives chromophores incorporated within oligoether acrylate photopolymer matrices [5]. Organic molecules like 2-methyl-4-nitroaniline (MNA), 2-(4-nitrophenyl)-(L)-prolinol (NPP) and N-(dimethylamino-5-nitro-phenyl) acetamide (DAN) have delocalized Π electron conjugation systems and are asymmetrized by the proton donor and acceptor groups which are highly polarized entities for NLO applications [6–8]. Parabens are esters of 4-hydroxybenzoic acid, only differ in the C-4 position of the ester groups such as methyl, ethyl, propyl or butyl-groups. Methyl-p-hydroxybenzoate (p-MHB), belongs to parabens group, is a stable and a non-volatile compound identified as a potential NLO material and also used as an antimicrobial preservative in foods, drugs and cosmetics [9,10]. Many researchers have reported the existence of different polymorphism of p-MHB [11–13] and some of the researchers successfully crystallized p-MHB from solution with different solvents, additives and also in gel medium [14–17]. In our previous work, we have reported that there was no polymorphic change when the p-MHB single crystals were grown from melt by conventional czochralski pulling method with different seeding techniques [18]. Therefore, naturally an interest arises to confirm whether there will be a possibility for a new polymorph to occur when the crystal is grown from top seeded solution growth (TSSG) method or not, since some of the previous reports revealed that there was the existence of temperature dependent polymorphism around the melting point [11,12]. Moreover, no report was previously available for the growth of this material through TSSG.

In the present work, as a newer approach, attempts were made to grow single crystal of p-MHB from melt by employing the TSSG method. Good optical quality single crystal of p-MHB was grown successfully. The grown single crystal was subjected to various characterization methods such as powder X-ray diffraction (PXRD), single crystal X-ray diffraction (SCXRD) and UV–Vis–near IR optical absorbance studies. The SHG efficiency of the grown p-MHB single crystal was determined by Kurtz-Perry powder technique.

2. Experimental procedure

2.1. Growth of p-MHB single crystal by TSSG method

In the top seeded solution growth (TSSG) method a specially

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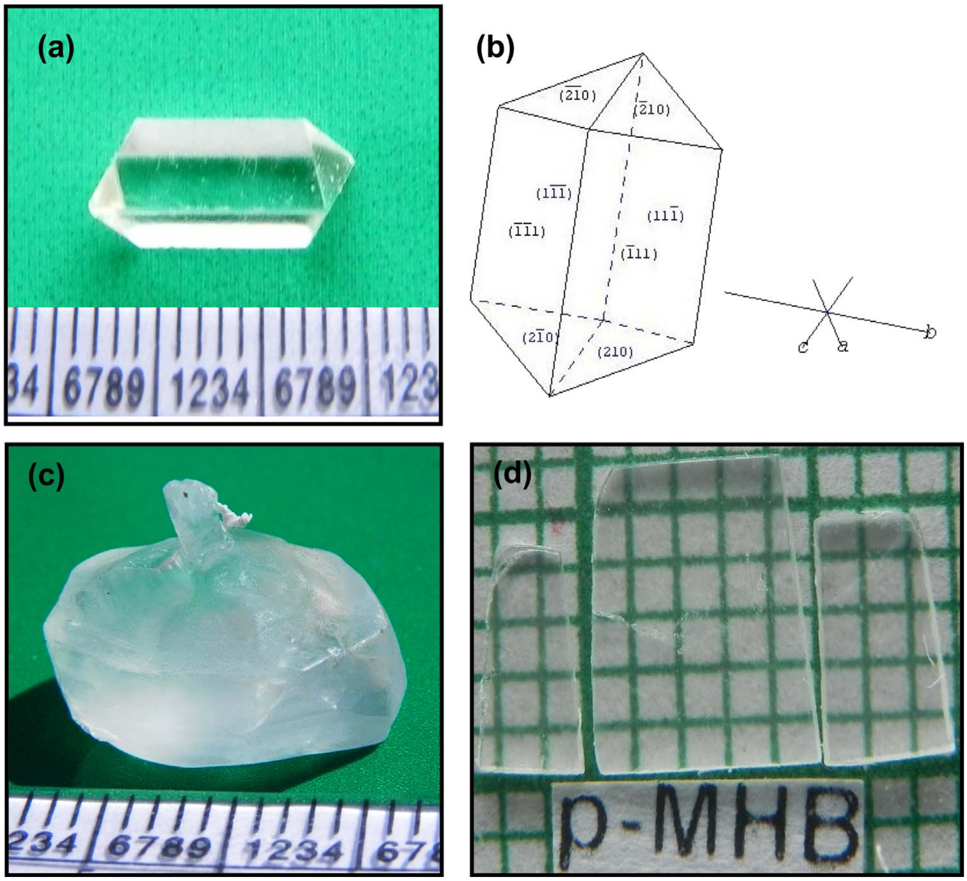

Fig. 1. (a) p-MHB seed crystal, (b) its morphology (c) grown bulk p-MHB single crystal by TSSG and (d) cross-sectional cut slices of the crystal.

designed mini-Czochralski type crystal puller along with a muffle furnace was used for growth. Seed rotation and pulling and lowering of the seed rod were carried out by a stepper motor controlled pulling head assembly attached to the crystal puller. Temperature of the furnace was controlled and maintained by suitable temperature controller which has the temperature controlling accuracy of ± 0.1 °C. A quartz crucible was used to melt the material and for the growth of the p-MHB crystal. The commercially available p-MHB salt (99% purity purchased from Himedia) was used for the preparation of the melt. About 20 g of p-MHB salt was taken in the quartz crucible, heated to 127 °C and congruent melt was obtained. A seed crystal of good quality was selected from the small dimensional single crystals previously grown from solution with methanol as solvent through spontaneous nucleation and grown by slow evaporation method at room temperature. Photograph of one such selected seed crystal with usual morphological features is shown in Fig. 1(a). The schematic of the morphology of the p-MHB seed crystal is shown in Fig. 1(b). The seed crystal was tied at the bottom tip of the stainless steel seed rod with the help of a *Teflon* tape. Then the seed crystal was suspended above the melt surface for seasoning at an elevated temperature for 3hrs. After the seasoning, the seed crystal was carefully introduced into the melt volume with slow rotation. Then the temperature of the molten solution was slowly reduced in such a way that the seed crystal was stable without showing any drastic dissolution or growth and it was kept at the same near the equilibrium condition for about 20 min for stabilization. Growth was initiated upon very small reduction in the temperature of the melt. Then the growth process was continuously carried out and monitored by employing appropriate cooling as well as crystal rotation rates throughout the experiment. After the achievement of reasonable size of the crystal within the melt volume, finally, the crystal was slowly pulled up above the melt surface and kept for seasoning again in order to avoid any thermal shock due to sudden temperature change during this transition. Then the temperature of the system was slowly reduced until the grown crystal reaches the room temperature. The experiment was tried with different types of seeds with different melt volumes at different crystal rotation and pulling rates. Finally all necessary parameters were optimized and good quality p-MHB single crystal was harvested.

2.2. Characterization

The grown p-MHB single crystal was subjected to powder X-ray diffraction studies carried out to demonstrate the crystallinity using Bruker D8 Advance X-ray diffractometer with Cu Kα (λ=1.5406 Å) radiation with scanning angle ranging from 10 to 40° in 2θ and a scan speed of 0.02° 2θ per second. SCXRD analysis of the grown crystal was carried out using Bruker D8 QUEST diffractometer with graphite-monochromated radiation (Mo Kα, λ=0.1707 Å). In order to identify the optical transparency of the grown single crystal, the optical absorption in the UV–Vis–Near IR region was recorded using the JASCO V-650 UV–Vis–near IR spectrophotometer. Second Harmonic Generation (SHG) efficiency of the grown crysal was analysed by Kurtz and Perry powder SHG technique [19]. In this technique, the grown single crystal of p-MHB was ground into fine powder with a uniform particle size of 150 µm, then packed into a sample holder of size ~1 mm bore and ~6 mm long and a laser beam of wavelength 1064 nm generated from Q-switched Nd: YAG laser with input beam energy of 3.45 mJ/pulse was exposed on the capillary. The second harmonic output energy was measured through a storageoscope and the relative SHG efficiency of p-MHB crystal was measured and compared with the inorganic standard KDP.