Growth of 2-amino-5-chlorobenzophenone single crystal by Microtube Czochralski method and its characterization

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Abstract. Organic single crystals of 2-amino-5-chlorobenzophenone (2A5CB) were grown by Microtube Czochralski method using Microtube as a seed. The grown crystals were characterized by single crystal and powder X-ray diffraction. The functional groups of the grown crystal were found using Fourier transform infrared spectroscopy. The cutoff wavelength of 2A5CB has been identified using UV-vis-NIR studies. Thermogravimetric/differential thermal analysis (TG/DTA) has been carried out to find the thermal behaviour. 2A5CB was found to be thermally stable up to 125°C. Powder second harmonic generation (SHG) was investigated to explore its nonlinear optical (NLO) properties. The mechanical stability of 2A5CB is studied by using Vickers hardness testing.

Keywords. Optical materials; crystal growth; mechanical properties; thermogravimetric analysis; X-ray diffraction; Czochralski method.

1. Introduction

Nonlinear optical (NLO) materials that are capable of generating the second harmonic frequency play an important role in the domain of optoelectronics and photonics. NLO materials have wide application in the field of telecommunication, optical computing and optical data storage. In the last decade, there has been tremendous progress in the development of the NLO materials having large NLO coefficients.^{1–5} NLO crystals should meet several requirements, such as large phase-matchable NLO coefficient, a wide optical window around the visible region, mechanical stability and a high damage threshold.⁶ Most of the organic materials will decompose below their melting temperature because of their thermal instability. Normally the Bridgman techniques are widely used to grow a bulk size crystal, but the impurity may be present in grown crystal and the orientation and nucleation cannot be controlled. However, in Microtube Czochralski technique the repeatability of getting single crystals is about 80% with the optimized growth parameters. Due to poor thermal conductivity of organic materials, a slight thermal fluctuation leads to more instability in solid-liquid interface in the conventional Czochralski technique whereas in Microtube Czochralski technique, Microtube is found to be improving the stability of solid/liquid interface at the initial stage of nucleation.⁷ From this technique we can control the nucleation and growth orientation in the Microtube by varying the parameters. 2-Amino-5-chlorobenzophenone (2A5CB) is an organic

material for NLO applications. 2A5CB has a molecular weight of 231.68. The molecular formula of 2A5CB is $C_{13}H_{10}ClNO$, which belongs to the C-face-centered monoclinic system. The difficulty of solution-grown crystals is that it is needle shaped and small sized, moreover it is not sufficient for second harmonic generation (SHG) studies. Ramesh Babu *et al*⁸ and Gulam Mohamed *et al*⁹ have reported the 2A5CB single crystal's cutoff wavelength as 440 and 390 nm, respectively. The cutoff wavelength of Microtube Czochralski-grown 2A5CB is 456 nm. The Microtube Czochralski was employed with the aim of growing a large size 2A5CB single crystal as well as justifying the suitability of this method for single-crystal growth. The grown crystal was subjected to single crystal and powder X-ray diffraction (XRD) studies, Fourier transform infrared spectroscopy (FT-IR), UV-vis-NIR studies, thermogravimetric-differential thermal analysis (TG-DTA) and microhardness studies.

2. Experimental

Figure 1 shows the schematic arrangement of the Microtube Czochralski method. A 55 mm ID and 70 mm height glass crucible was placed in the Kanthal wire-wound furnace. The stainless steel (SS) Microtube was fitted with a rod which can be rotated. A SS Microtube of 6 μ m ID has been used for seeding the melt. The temperature profile was taken before loading the material in glass crucible. The high purity source material was directly purchased from Alfa Aesar and the material was first loaded into the glass crucible, then it was heated up to 105°C. After attaining the visible melt, the SS Microtube was just kept above the melt surface in order

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Figure 1. Microtube Czochralski method.

to attain the thermal equilibrium condition. Once the attainment of thermal equilibrium is ascertained, the microtube was brought in contact with the melt. The temperature was reduced at a predefined rate until growth occurred. A fine column of melt was rising inside the microtube because of the capillary rise. It was allowed to crystallize inside the microtube and then used as a primary seed. Melt that wets the walls of the fine capillary tube, rises to a height depending upon the tube radius and the surface tension of the melt. The pulling rate of the microtube and growing rate of the crystal are carefully optimized in order to get perfect crystal. During the initial growth period the control parameters, such as temperature and pulling rate, were carefully monitored. The resulting crystal diameter depends on the pulling rate and temperature gradient. High pulling rate with a small temperature gradient yields a smaller diameter crystal, whereas large gradient and low pulling rate results in a thicker sample. Once the growth run is completed, the system temperature is reduced at a predetermined cooling rate.^{7,10} The optimized experimental parameters in this present investigation for the growth of 2A5CB are as follows: pulling rate 1–2 mm h⁻¹; seed rotation rate 8 r.p.m.; cooling rate 1°C h⁻¹ and the axial thermal gradient 8°C cm⁻¹. Figure 2 shows the grown crystal of 2A5CB.

Figure 2. 2-Amino-5-chlorobenzophenone single crystal.

Figure 3. Powder XRD pattern of 2A5CB.

3. Characterization studies

3.1 Single-crystal XRD analysis

From the single-crystal XRD measurement, it is found that the grown crystal belongs to the C-face-centered monoclinic system. The determined lattice parameters are $a = 9.75$ Å, $b = 18.99$ Å, $c = 24.81$ Å and $\alpha = \gamma = 90^\circ$, $\beta = 95.78^\circ$ and volume = 4569.29 Å³.

3.2 Powder XRD

Powder XRD studies were carried out using CuK α (1.54058 Å) radiation, scanning angle ranging from 10° to 40° at a scan rate 1° min⁻¹ to study the phase purity of the grown crystal. The XRD pattern of 2A5CB is shown in figure 3. The obtained peaks are indexed. The sharp peaks show the crystalline nature of the sample.

Figure 4. FT-IR spectrum of 2A5CB.

3.3 FT-IR analysis

Figure 4 shows the FT-IR spectrum of 2A5CB. The spectrum was recorded in the range of 4000–400 cm^{-1} . The absorption at 3420 and 3320 cm^{-1} is due to N–H stretching vibration. The N–H group normally gives rise to one band and NH_2 group gives two bands, such as symmetrical and antisymmetrical stretching. The absorption peak at 1620 cm^{-1} corresponds to C=O stretching vibration of the carbonyl group. The presence of aromatic amines stretching is confirmed at 1240 cm^{-1} . The aromatic ring of C=C is revealed at 1468 and 1535 cm^{-1} . The peaks at 828 and 950 cm^{-1} are due to C=C–H out of plane. The peak at 763 cm^{-1} corresponds to C–Cl stretching vibration.

3.4 UV-vis-NIR studies

The grown 2A5CB single crystal was cut and polished, and the good transparent crystal with 3 mm thickness was used for UV-vis-NIR studies. These studies were carried out without any antireflection coatings. The recorded spectrum is shown in figure 5. It is observed that the grown 2A5CB single crystal has the transparency of around 50% and the cutoff wavelength is around 456 nm, whereas solution-grown crystal gives higher transmittance. The lower transmittance is due to the dislocations present in the melt-grown crystal.

3.5 Thermal studies

The results obtained from TG and DTA are shown in figure 6. The TGA and DTA traces of 2A5CB were recorded in the nitrogen atmosphere at a scanning rate of 10°C min⁻¹ from room temperature to 250°C. The grown 2A5CB crystal was stable upto 125°C. As shown in figure 6, a sharp endothermic peak was observed at 101.5°C, which is assigned as the melting point. A sharp peak indicates the good degree of crystallinity of the sample. In the TGA analysis, there is a gradual and continuous weight loss beyond 125°C. From

Figure 5. UV-vis-NIR spectrum of 2A5CB.

Figure 6. TG-DTA curve of 2A5CB.

these results it is concluded that there is no phase change observed in the crystal.

3.6 Microhardness studies

Information about mechanical hardness of NLO crystals is important not only from the device point of view, but also due to the close correlation between mechanical hardness, bond strength, laser damage, etc.^{11–13} Figure 7 shows the load dependence of hardness of 2A5CB. From the plot it is clear that Vickers hardness number (VHN) increases with load. This indicates the reverse indentation size effect (ISE). The measurement performed beyond a load of 100 g resulted in some cracks. The hardness behaviour of solution-grown crystal is found to be opposite to hardness behaviour of melt-grown crystal. The defects due to solution inclusion (in solution-grown crystals) reduce the hardness. The defects in melt-grown crystal increase the hardness as they cause resistance to lattice slipping.

Figure 7. Vickers microhardness test of 2A5CB.

3.7 SHG efficiency

The Kurtz–Perry powder technique is an extremely valuable tool for SHG. The ground powder was packed in a triangular cell and kept in a cell holder. A Q-switched Nd-YAG laser beam of wavelength 1064 nm with the energy of the laser pulse around 4.7 mJ was allowed to strike the sample cell normally. The beam emerging through the sample was focused on to a Czerny-tuner monochromator using a pair of lenses. The detection was carried out using a Hamamatsu R-928 photomultiplier tube. The signals were captured with an Agilent infiniiium digital storage oscilloscope interfaced to a computer. The monochromator is set at 532 nm. NLO signal is captured by the oscilloscope through the photomultiplier tube. The intensity of the green emission is estimated to be as 0.3 times that of the reference KDP sample.

4. Conclusion

2A5CB single crystal was successfully grown by the Microtube Czochralski method. The grown crystal was characterized by single-crystal XRD, FT-IR and PXRD. The grown crystal belongs to C-face-centered monoclinic system, which is confirmed with single-crystal XRD studies. The material was stable up to 125°C and it shows there is no phase change present in the melt-grown crystal. The UV–vis–NIR study

shows the cutoff wavelength as 456 nm and its transmittance is 50% in the vis–NIR region. This is moderately good for melt-grown crystals. The SHG efficiency of 2A5CB is 0.3 times that of KDP. Microhardness studies indicate the occurrence of reverse indentation size effect in the grown crystal. Finally, we claim that the Microtube Czochralski is suitable technique for growing a large single crystal without a seed. Due to its versatility and repeatability of getting bulk single crystals, this method can also be extended to grow other newer materials.

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