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Investigation on the SR method growth, etching, birefringence, laser damage threshold and thermal characterization of strontium bis (hydrogen L-malate) hexahydrate single crystal

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ABSTRACT

Optically good quality, semi-organic bulk single crystal of strontium bis (hydrogen L-malate) hexahydrate (SrLM) was successfully grown by Sankaranarayanan–Ramasamy (SR) method. Transparent ⟨0 1 0⟩ oriented unidirectional bulk single crystals of diameters 10 and 20 mm and length maximum up to 70 mm were grown over the growth period of 34 days with growth rate of 1 mm/day by the SR method. The grown crystals were subjected to various characterization studies such as chemical etching, UV–vis NIR spectrum, birefringence, laser damage threshold and thermal analysis (TG/DTA). The quality was also ascertained by birefringence studies.

1. Introduction

Nonlinear optical (NLO) crystal for the UV–visible region is extremely important for laser spectroscopy and laser processing. Hence, it is important to search for new NLO material, which possesses large NLO coefficient, shorter cutoff wavelength, transparency in the UV region and higher laser damage threshold [1–3]. In recent years the search for new nonlinear optical materials included semi-organic and coordination compounds due to their advantages over traditional inorganic and organic compounds. Semi-organic materials possess several attractive properties such as high damage threshold, wide transparency range, less deliquescence and high nonlinear coefficient, which make them suitable for frequency doubling. Dicarboxylic acids have attracted the specific attention of many researchers for long time due to their overwhelming practical applications in science and technology. The growth and characterization of metal complexes of dicarboxylate crystals like oxalates, malonates, maleates and substituted acids like tartrates and lactates [4–7] caught major attention due to their optical and ferroelectric properties. Previous studies on organic and semi-organic crystals have shown that L-malic acid ($C_4H_6O_5$) is one of the simplest chiral dicarboxylic acids, is a suitable building block in crystal engineering. Its chirality ensures the absence of a center of symmetry, essential for optical nonlinear second harmonic generation. L-malic acid, used as a means for creating two dimensional anionic networks held together by O–H…O hydrogen bonds [8,9], urea L-malic acid, ammonium malate, zinc malate 1,10-phenanthroline and cesium hydrogen malate are the famous reported semi-organic malic acid family crystals [10–13]. In this series, SrLM single crystal is an excellent candidate for SHG applications in the malic acid family. The low-temperature solution growth is an important technique because large-size nonlinear optical and other crystals are being grown by this technique. The growth of bulk single crystals without defects is a challenging task for crystal growers. Also for SHG applications, phase-matchable crystals are needed where the specimen should have optimum size along the particular direction [14]. From this point of view, Sankaranarayanan–Ramasamy method [15] is suitable to grow high quality and large size single crystals from solution. The earlier report by de Matos Gomes et al. [16] dealt with the crystal structure of SrLM and limited studies like SHG. SrLM was grown by conventional slow cooling technique and SR method and their optical, dielectric, mechanical and SHG studies were investigated [17]. In the present paper, 70 mm length and 20 mm diameter ⟨0 1 0⟩ SrLM crystal was grown by SR method. The structural perfection and growth features of SrLM were analyzed by chemical etching studies. The grown crystals were characterized by UV–vis NIR spectrum, birefringence, laser damage threshold and Thermal analysis (TG/DTA).

2. Experimental

2.1. Crystal growth

The growth of SrLM single crystals was carried out by low temperature solution growth technique by conventional slow

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cooling and unidirectional solution growth by the SR method. Details of synthesis and crystal growth of SrLM by slow cooling method were described by us elsewhere [17]. It is necessary to increase the purity to a reputable level by successive recrystallization process and the maximum attention has been paid to high purity SrLM during the synthesis. The materials purifications and the prepared SrLM solutions are in identical condition for conventional and SR crystal growth experiments. After the completion of the growth run, optically transparent crystal of $14 \times 6 \times 6\ mm^3$ was harvested (Fig. 1(a)) by conventional slow cooling technique.

Based on the morphology of the conventional method grown SrLM crystal, the (0 1 0) face was selected in the SR method to impose the orientation in the growing crystal. According to the chemical bonding theory of single crystal growth [18,19], the anisotropic origin of growth morphology is from crystal structure, kinetic control thus becomes tremendously important in producing high quality single crystals [20]. The 2 mm thickness of b-cut SrLM crystal was prepared from conventional method. After polishing, a thin plate of SrLM, it was mounted at the bottom of the glass ampoule and the (0 1 0) face was selected for the uniaxial growth. The saturated solution of SrLM was carefully poured in the glass ampoule and kept into water bath at constant temperature. A ring heater positioned at the top of the growth ampoule was connected to the RTD temperature controller providing 37 °C for solvent evaporation. The placement of ring heater at the top of the saturated solution also controls the spurious nucleation near the surface region of the solution during the entire growth period. The rate of evaporation was controlled by small hole in thin plastic sheet which covered the top of the glass ampoule that allows passage of vapors and avoids contamination of the solution. Controlled evaporation also helps in achieving the uniform growth rate. The temperature controller around the growth region is maintained at 34 °C with ± 0.1 °C accuracy. In SR method the growth is performed at a constant temperature with long range stability. The growth conditions were closely monitored and within two days, slight dissolution is observed at the surface of the seed crystal. The size of the seed crystal started increasing within five days. Due to the gravity induced concentration all the solute molecules are approaching the crystal surface directly and therefore the surface attracts more atoms easily [15]. Due to the transparent nature of the solution and the experimental setup, real-time close-up observation revealed solution–crystal interface, which was found to be flat. Under optimized condition highly transparent crystal growth was achieved. The shape of solution–crystal interface was monitored during growth process. We found that the seed crystal started to grow after 12 days with growth rate of 1 mm/day. A thin layer of solution is always seen between the growing crystal and the ampoule. This indicates that the crystal is not stressed by the ampoule. By this method, crystal with the diameters 10 mm and 20 mm and length maximum up to 70 mm were grown in a period of 34 days (Fig. 1(b)). The cut and polished wafers of 10 mm diameter and 20 mm diameter of SrLM single crystals are shown in Fig. 1(c) and (d), respectively. No microbial contamination is observed in the growth solution of SrLM even when solutions are kept for a long time. There is no fragility in SR method grown SrLM wafers as observed during the process of cutting and polishing.

2.2. Characterizations

The comparative characterizations have been made on SEST and SR method grown SrLM crystals. Samples were prepared with the similar (0 1 0) facet and identical thickness. The surface damage is affected by the energy absorbing defects such as strains, scratches and polishing contaminants which influence the physical properties strongly. Therefore the experiments are performed on the highly polished SrLM crystals thus minimizing any surface defects. In order to confirm the reproducibility, every characterization was repeated several times and the similar results have been observed. The chemical etching analysis was carried out using an OLYMPUS U-TV0.5XC-3 optical microscope in the reflection mode. The UV–vis NIR spectrum of the SrLM crystal was recorded at room temperature using a Perkin-Elmer 35 spectrophotometer using cut and polished wafer of the SR method grown (0 1 0) face of crystal of 3 mm thickness with slit width of 2 nm and scan speed of 240 nm/min (range 200–1100 nm). The light

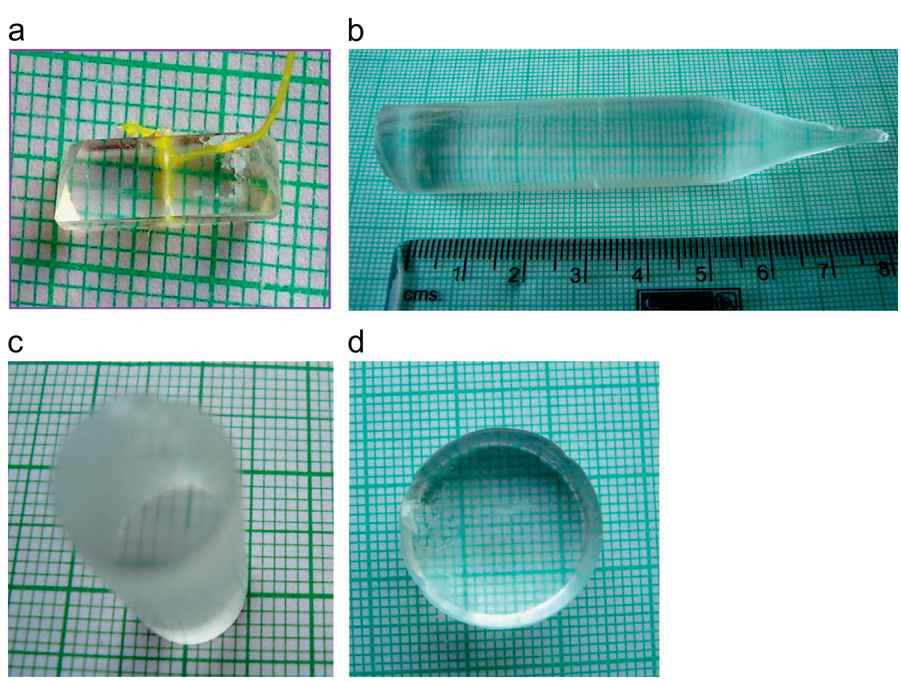

Fig. 1. (a) Slow cooling method grown SrLM crystal, (b) SR method grown SrLM crystal. (c) Cut and polished 10 mm thick and 10 mm diameter wafer of SrLM. (d) Cut and polished wafer of 20 mm diameter SrLM crystal grown by SR method.