

Design of a solution crystal growth crystallizer with a versatile electronic reciprocal motion control for a crystals holder

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A description of a modified crystallizer for growing large crystals from solutions along with the design of a versatile electronic reciprocating control system to change and reciprocate the motor speed containing the seed holding rod for solution growth crystallizer is presented. In this system, rotation rate and number of revolutions in the clockwise and counter clockwise direction can be adjusted as and when desired. This electronic system alleviates the problem of jerky motion of seed holder during reciprocation as in earlier mechanical systems. Good quality crystals of important nonlinear optical materials such as Methyl-(2,4-dinitrophenyl)-aminopropanoate: 2-Methyl-4-nitroaniline (MNA:MAP), L-Arginine Phosphate (LAP) L-Histidine tetrafluoroborate (LHFB), L-Arginine tetrafluoroborate (LAFB) and others have been successfully grown using this system. The complete crystallization apparatus along with electronic circuit can be easily fabricated with readily available components by graduate and undergraduate students.

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1 Introduction

The growth of crystals from low temperature solutions occupies a prominent place especially when materials are not stable at elevated temperatures. A number of concepts for solution crystal growth systems are found in literature [1]. One of the best concepts for growth of both inorganic and organic crystals from solution is by temperature lowering of solution, provided the material has positive temperature coefficient of solubility. In this method, a saturated solution of the material to be grown, is prepared at a chosen temperature and kept at this temperature for 24 hours. Then the seed holding rod is inserted in the growth chamber and its rotation is initiated. The growth process is initiated by lowering the temperature slowly. The temperature of the solution is lowered at a pre-programmed rate typically 0.05K to 2.0K per day depending on the solubility of the chosen material. The complete crystallization process may take from a week to several weeks. To terminate the growth process the grown crystals are taken out of the solution without the thermal shock.

A solution crystal growth is a highly complex process and depends on various growth parameters such as quality of seed, temperature of growth, temperature lowering rate, character of solution, seed rotation and stirring of solution besides other conditions. To grow good quality crystals, above cited parameters have to be optimized for each crystal.

2 Experimental

A schematic diagram of a modified solution crystal growth system designed and fabricated in our laboratory is shown in Fig. 1 after designing number of crystallizers [2-4] in our laboratories. A 250 ml crystallizer jar (4), which holds the growth solution, is placed inside a 2.5 liter jacketed kettle (3). The linear and reciprocating motion of the Teflon seed holder (5) is controlled by a rack-pinion arrangement (8) and electronic circuit (7) respectively. A reversible motor (6) is used for rotating the seed holder. The temperature of the growth solution is controlled and programmed by circulating water using NesLab bath (1). To prevent evaporation of the solvent specially designed oil Teflon seal (3) and RTV/Teflon seal (3) are used. The main features of our

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crystal growth system are: (i) better temperature stability even with sudden fluctuations in room temperature, (ii) better control over evaporation of organic solvents, (iii) a mechanical screw type arrangement for pulling the seed crystal at a controlled rate, (iv) the possibility of varying the seed orientation and type, and (v) a versatile electronic reciprocating control system to change and reciprocate the motor speed containing the seed holding rod.

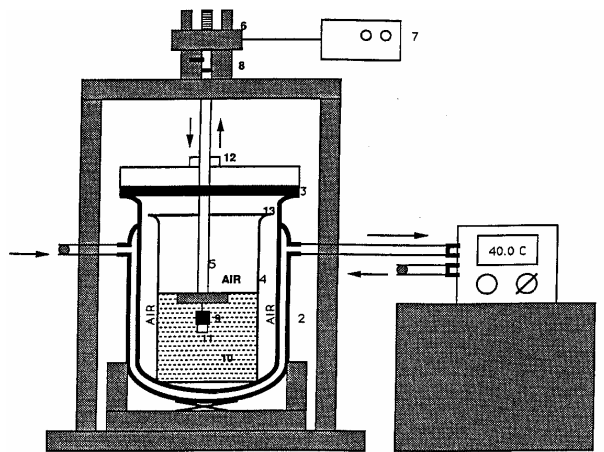


Fig. 1 Design for a new crystallizer for growing organic crystals. (1) Circulating bath; (2) Jacked reaction kettle; (3) RTV/Teflon seal; (4) Crystallizer jar; (5) Teflon seed holder; (6) Reversible motor; (7) Circuit for reciprocating and controlling the stirring rate of seed holder; (8) Arrangement for pulling the crystal during growth; (9) Teflon tape cover; (10) Solution; (11) Seed crystal; (12) Teflon seal; (13) Glass lid.

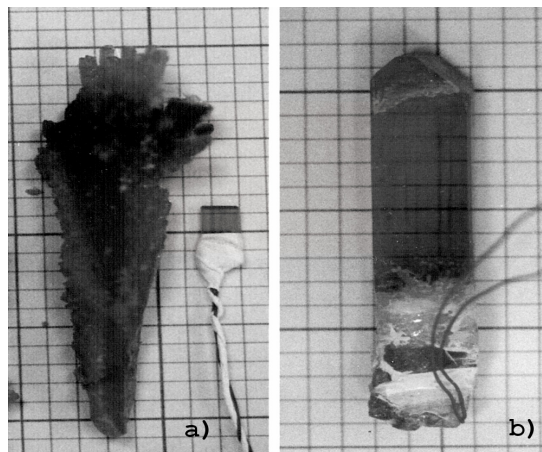


Fig. 2 The Photographs of MNA:MAP seed and aloe vera-tree type growth (a), without aloe vera-tree type growth (b)

Better temperature stability was accomplished by loading the growth solution in a beaker kept inside the jacketed vessel. An air gap provides extra insulation. Moreover, spontaneous nucleation at the bottom of the growth vessel, which hampers the growth and the crystal yield, is completely eliminated. By providing an extra lid on the inside beaker and a Teflon seal over the jacketed vessel, the evaporation of the solvent was reduced dramatically. The inner beaker is filled halfway with solution rather than three-fourth as unlike normal methods, and the growing crystal is pulled in a controlled fashion. The filling of the inner beaker, to three-fourth, is not required. In this way not only is the crystal annealed in situ but also spurious aloe vera-tree like growth near the seed in some crystals such as MNA:MAP, is greatly reduced or completely eliminated. Fig. 2 (a) shows the seed crystal along with MNA:MAP crystal grown using usual technique i.e. without pulling the growing crystal. Fig. 2(b) shows the same crystal grown with pulling and aloe vera-tree type growth is avoided. Furthermore, large crystals can be grown from a smaller amount of expensive mother liquor as the crystal is pulled while growing.

Besides temperature control, the uniform rotation of seeds is required so as not to produce stagnant regions or re-circulating flows, otherwise inclusions in the crystals will be formed. To study and achieve uniform and optimum transport of solute to the growing crystals, various seed rotation mechanisms have been used in the past [2-5]. The unidirectional rotation of the seed leads to the formation of cavities in central regions of a crystal face because of lesser solute transport than edges and corner of the growing crystal. Furthermore, non-uniform solute supply favors the formation of thick layers which subsequently lead to the trapping of inclusions and to generate dislocations. Periodic rotation of the growing crystal in opposite directions suppresses edge formation but does not eliminate the formation of central cavity. To avoid these defects and stagnant regions of solution, eccentric or clock-wise and counter clockwise motion of the seed holder is used in growing crystals from solutions. A few mechanisms [2-5] have been used in the past, to generate reciprocating motion of the seed holder such as electro – mechanical [3] and rack-pinion [4]. In the electro-mechanical system, a connection of the motor polarity is reversed mechanically by using a micro-switch. In this mechanical system, there is a jerky motion on reversal, which sometimes causes seeds to fall down. The jerky motion also creates a turbulent flow in the fluid and hence non-uniform transfer of solute to the growing faces, thereby defective crystals may be formed. The micro-switch has to be changed frequently due to mechanical

failure. Furthermore, effect of seed rotation rates on the growth rate and the quality of the crystals can not be systematically studied. It is because rotation rate cannot be varied. In the rack-pinion arrangement, there is no jerking motion but one has to change gears to change rotation and reversal rate, which is quite an involved process.

To improve on these drawbacks, in our Crystal Growth Laboratory at Alabama A&M University, a versatile solid state electronic circuit for reciprocating the direction of the seed holder is designed along with added features such as facility to vary rotation rate, stopping time on reversal and time for clockwise and counter clockwise motion of crystal/seed holder. These designed features will allow the crystal growers to study more decisively the effect of seed rotation rates on the growth and quality of the grown crystals, thereby optimizing this important parameter for growing better quality crystals.

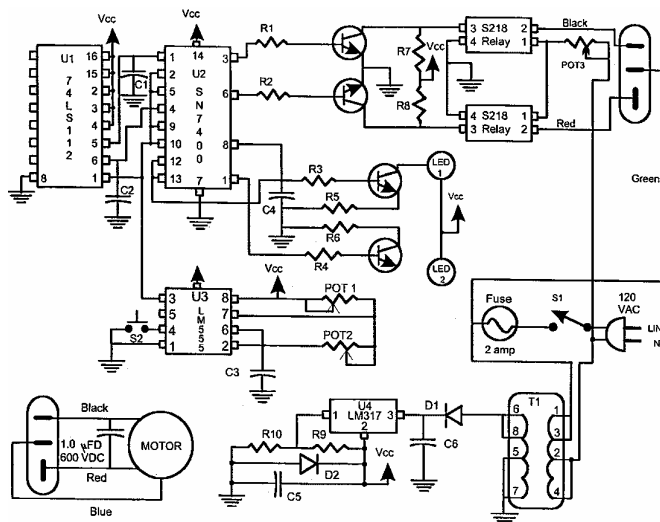


Fig. 3 The Electronic circuit diagram for reciprocating motion of seed holder for solution growth crystallizer.

A schematic diagram of the basic electronic circuit for reciprocating motion control is shown in Fig. 3. In Fig. 3, the timer (Chip LM 555, U3) produces square wave timing pulse. It may be set for a particular frequency (POT1) and duty cycle (POT2) in combination with timing capacitor (C3), and reset if necessary by switch (S2). The timing wave form is divided by the J-K flip flop chip 74LS112 (U1) to one half the timer frequency. Parasitic oscillations are suppressed by capacitors (C1, C2 and C4). The two wave forms are combined by NAND gates chip SN7400 (U2) to alternately turn on the transistor (Q1 and Q2) to control the solid state relays (1 and 2) which connect the alternate sides of the motor capacitor to the 110 VAC return line. Similarly, the transistor (Q3 and Q4) alternately turn on the indicator lamps (LED1 and LED2).

Current limiting and bias is provided by resistors (R1 through R8). Motor rotation speed is controlled by potentiometer (POT3). A power supply consisting of the step down transformer (T1), Voltage regulator (U4) and associated filtering circuit (D1 and D2, C5 and C5), and voltage setting divider (R9 and R10) provides 5 VDC to the circuit. The operation of the circuit causes the following sequence of states in the system: during first interval, the seed holder motor runs counter clockwise; during next interval, the motor comes to a stop; during next interval, the motor runs clock wise; and during next interval, the motor again comes to stop. Then the entire cycle of operation in repeated, and the intervals can be varied as needed for a particular crystal growth experiment.

3 Results and discussion

Various new nonlinear optical crystals which holds promise for their use in nonlinear optical devices such as L-arginine phosphate, L-Histidine tetrafluoroborate, L-arginine tetrafluoro borate, Methyl-(2,4-dinitrophenyl)-aminopropanoate: 2-Methyl-4-nitroaniline (MNA:MAP) and L-pyroglutamic acid of high quality have been grown using above mentioned reciprocating system, by temperature lowering technique described elsewhere [6-10]. In the investigator's observation and experience, there is definite improvement in the quality of grown crystals and success rates of the growth runs, which is evident from the transparency and less scattering under

laser illumination. This reciprocal motion control electronic system for solution growth crystallizers has been in use in our laboratory for several years, and is working satisfactorily.

It is worthwhile to mention that this simple and versatile crystallization apparatus can be fabricated in any college or university or scientific laboratory from readily available components. Besides its use in physics or chemistry laboratory experiments, it can also be used for doing extensive research on the effect of important parameters such as seed rotation rate, stopping time of reversal, and number of rotation in clockwise or counter clockwise direction on the quality and growth rate of technologically important crystals.

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