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Investigations on the Growth and Characterization of Nonlinear Optics (NLO) Single Crystals

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Abstract:

Nonlinear optics (NLO) single crystals are materials that exhibit strong nonlinear optical properties and are critical for the development of various optical applications. The growth and characterization of NLO single crystals play a significant role in determining their optical and physical properties. The growth process involves melting the starting material and cooling it to form a single crystal. The resulting crystal's quality is dependent on various factors such as the purity of the starting material, the growth rate, and the control of the crystal's morphology. Characterization techniques commonly used include X-ray diffraction, Fourier transform infrared spectroscopy, UV-Visible spectroscopy, and second harmonic generation. These techniques provide information on the crystal's structure, orientation, molecular structure, optical properties, and nonlinear response. Overall, the growth and characterization of NLO single crystals are critical for the development of various applications that rely on the strong nonlinear optical properties of these materials.

Keywords: Characterization, growth, Nonlinear optics , single crystals, UV-Visible spectroscopy, X-ray diffraction

Introduction:

Nonlinear optics (NLO) refers to the study of the optical properties of materials that exhibit a nonlinear response to electromagnetic radiation. This nonlinearity is a result of the interaction between the incident light and the material, leading to second or higher harmonic generation, frequency mixing, and other nonlinear effects.

NLO single crystals are materials that exhibit strong nonlinear optical properties and are commonly used in a variety of applications, including frequency conversion, optical communication, and laser technology. The growth and characterization of NLO single crystals are critical for the development of these applications.

Growth of NLO Single Crystals:

The growth of NLO single crystals can be achieved by various methods, including the Czochralski method, the Bridgman method, and the vertical gradient freeze (VGF) method. In general, the growth process involves the melting of the starting material, followed by the controlled cooling to form a single crystal.

During the growth process, it is important to maintain a uniform temperature and avoid the introduction of impurities. The quality of the resulting crystal is dependent on various factors such as the purity of the starting material, the growth rate, and the control of the crystal's morphology.

Characterization of NLO Single Crystals:

Characterization of NLO single crystals is critical to determine their optical and physical properties. The characterization techniques commonly used include:

X-ray Diffraction (XRD): This technique is used to determine the crystal structure and orientation of the NLO single crystal. X-ray diffraction analysis can provide information on the lattice parameters, symmetry, and the degree of crystalline perfection of the crystal.

Fourier Transform Infrared Spectroscopy (FTIR): FTIR is a technique used to determine the molecular structure of the NLO single crystal. The infrared absorption spectrum provides information about the vibrational modes of the crystal, which are related to the chemical bonds in the crystal.

UV-Visible Spectroscopy: UV-Visible spectroscopy is used to determine the optical properties of the NLO single crystal. The absorption spectrum can provide information on the bandgap and other electronic properties of the crystal.

Second Harmonic Generation (SHG): SHG is a technique used to measure the nonlinear optical properties of the NLO single crystal. The technique involves the generation of a second harmonic wave at twice the frequency of the incident light, which is a measure of the crystal's nonlinear response.

Buckley (1951) has elegantly put the matter, “It should be remembered that, in the preparation of large crystals, the touch of the artist is about as important as the application of established scientific principles".

Scope and Objectives

The search and design of high efficient nonlinear optical (NLO) crystals for visible and ultraviolet (UV) regions are extremely important for laser and material processing. The inorganic, organic nonlinear optical materials have their advantages and disadvantages. The inorganic nonlinear optical crystals are easy to grow. They can be grown in to large sized crystals using the conventional solution growth technique. But the efficiency of the inorganic crystals is lower compared to their organic counterparts. The mechanical strength of inorganic crystals is high generally. The organic materials are difficult to grow and have less mechanical strength. Inspite of these drawbacks, the organic materials have high nonlinear activity. In order to combine the advantages of organic and inorganic materials, semiorganic crystals were grown.

In recent years, efforts have been made to synthesize amino acid mixed organic-inorganic complex crystals, in order to improve the chemical stability, laser damage threshold, linear and nonlinear optical properties.

In the present work the amino-acid L-valine has been selected and its organic-inorganic complexes have been synthesized using slow evaporation solution growth technique at low temperature. The aim of the present study is to identify novel NLO materials using L-valine.

Dicarboxylic oxalic acid has been incorporated with potassium hydroxide to explore their NLO properties. Semiorganic crystals of Potassium hydrogen oxalate and Magnesium sulphate doped in Potassium borooxalate have been grown using slow evaporation solution growth technique at low temperature.

1. The present investigation is aimed at:
2. Growing bulk sized crystals.
3. Identifying and solving the crystal structure by XRD single crystal diffraction analysis.
4. Analysing the grown crystal for its percentage elemental composition, optical transmission/absorption, NLO property, laser damage threshold, hardness, dielectric property, and photoconductivity.
5. Studying the thermal behaviour of the grown crystals.

Techniques of Crystal Growth

The methods of growing single crystals may be classified according to their phase transformation as given below:

Growth from solid → solid - solid phase transformation

Growth from liquid → liquid - solid phase transformation

Growth from vapour → vapour - solid phase transformation

The basic common principle in all these methods is that a nucleus is first formed and it grows into a single crystal by organizing and assembling ions or molecules with specific interactions and bonding, so that the process is slow and multiple nucleations is minimized.

Growth from Melt

Growth from melt is by far the fastest of the growth methods, as its rate does not depend on mass transport process. All materials can be grown in single crystal form from the melt provided they melt congruently without decomposition at the melting point and do not undergo any phase transformation between the melting point and room temperature. The growth from melt can be further subdivided into the following techniques:

- Bridgman technique
- Czochralski technique
- Kyropoulos technique
- Zone melting and Normal Freezing technique
- Verneuil technique

Gel Growth

The growth of single crystals in gel is a self -purifying process free from thermal strains which are common in crystals grown from the melt. Crystal growth in gels is a promising technique for growing single crystals of substances which are slightly soluble in water and which cannot be grown conveniently from melt or vapour. The gel method has also been applied to study the crystal formation in urinary calculi and rheumatic diseases. Based on the nature of physical changes and chemical reactions involved in the growth process, gel method can be classified into four categories:

- Chemical reaction method
- Chemical reduction method
- Solubility reduction method
- Complex dilution method

Growth from Vapour

This is a method by which single crystals and epitaxial layers of high chemical purity and crystalline perfection may be obtained. The thickness and the doping of the layers can be closely controlled and the process can be recycled. But since the growth is slow, the method is not practical for bulk single crystals. Growth from vapour phase may generally be subdivided into two categories:

1. Physical vapour transport
2. Chemical vapour transport

Growth from Solution

Materials, which have high solubility and have variation in solubility with temperature, can be grown easily by solution method. There are two methods in solution growth depending on the solvents and the solubility of the solute. They are

- High temperature solution growth
- Low temperature solution growth

Three principal methods are used to produce the required supersaturation.

1. Slow cooling of the solution
2. Slow evaporation of the solvent
3. The Temperature gradient method.

Optimizing Solution Growth

The growth of good quality single crystals by slow evaporation and slow cooling techniques require the optimized conditions and the same may be achieved with the help of the following norms: (i) Material purification, (ii) Solvent selection, (iii) Solubility, (iv) Solution preparation, (v) Seed preparation, (vi) Agitation, (vii) Crystal habit.

Material purification

An essential prerequisite for success in crystal growth is the availability of the highest purity material. Solute and solvents of high purity are required, since impurity may be incorporated into the crystal lattice resulting in the formation of flaws and defects. Sometimes impurities may slow down the crystallization process by being adsorbed on the growing face of the crystal which changes the crystal habit. A careful repetitive use of standard purification methods of recrystallization followed by filtration of the solution would increase the level of purity.

Solvent selection

A solution is a homogeneous mixture of a solute in a solvent. Solute is the component, which is present in a smaller quantity and the one which gets dissolved in the solvent. For a given solute, there may be different solvents. The solvent must be chosen taking into account the following factors to grow crystals from solution: (i) a good solubility for the given solute, (ii) a good temperature coefficient of solute solubility, (iii) less viscosity and less volatality, (iv) less corrosion and non-toxicity and (v) cost effective.

It is known that the choice of solvent provides some control over crystal habit and this effect depends on the interaction of the surface of the crystal as it grows and the solvent molecules. Solvents commonly used include light water (H_2O), heavy water (D_2O), ethanol, methanol, acetone, carbon tetrachloride, hexane, xylene and many others. Almost 90% of the crystals produced from low temperature solutions are grown by using water as solvent as water has high dielectric constant, stability, low viscosity, low toxicity and abundant availability.

Solubility

Solubility of the material in a solvent decides the amount of the material, which is available for the growth and hence defines the total size limit. If the solubility is too high, it is difficult to grow bulk single crystals and lower solubility restricts the size and growth rate of the crystals. Solubility gradient is another important parameter, which dictates the growth procedure. Neither a flat nor a steep solubility curve will enable the growth of bulk crystals from solution. If the solubility gradient is very small, slow evaporation of the solvent is the other option for crystal growth to maintain the supersaturation in the solution. Low temperature solution growth is mainly a diffusion-controlled process; the medium must be less viscous to enable faster transfer of the growth units from the bulk solution by diffusion. Hence, a solvent with less viscosity is preferable. Supersaturation is an important parameter for the solution growth process.

The solubility data at various temperatures are essential to determine the level of supersaturation. Hence, the solubility of the solute in the chosen solvent must be determined before starting the growth process. The solubility of the solute can be determined by dissolving the solute in the solvent maintained at a constant temperature with continuous stirring. On reaching saturation, equilibrium concentration of the solute can be determined gravimetrically. A sample of the clear supernatant liquid is withdrawn by means of a warmed pipette and a weighed quantity of the sample is analyzed. By repeating the above procedure for different temperatures, the solubility curve can be plotted. Solubility of most substances increases with temperature (the temperature coefficient of solubility is positive).

Solution preparation and crystal growth

For solution preparation, it is essential to have the solubility data of the material at different temperatures. Sintered glass filters of different pore size are used for solution filtration. The clear solution, saturated at the desired temperature is taken in a growth vessel. For growth by slow cooling, the vessel is sealed to prevent the solvent evaporation. Solvent evaporation at constant temperature can be achieved by providing a controlled vapour leak. A small crystal suspended in the solution is used to test the saturation. By varying the temperature, a situation where neither the occurrence of growth nor dissolution is established. The test seed is replaced with a good quality seed. All unwanted nuclei and the surface damage on the seed are removed by dissolving at a temperature above the saturation point. Growth is initiated after saturation. Solvent evaporation can also be helpful in initiating the growth.

Seed preparation

Seed crystals are prepared by self-nucleation under slow evaporation from a saturated solution. Seeds of good visual quality, free from any inclusion and imperfections are chosen for growth. Since, strain free refaceting of the seed crystal results in low dislocation content, a few layers of the seed crystal are dissolved before initiating the growth. Defects present in an imperfect seed propagate into the bulk of the crystal, which decreases the quality of the crystal. Hence, seed crystals are prepared with care. The quality of the bulk crystal is usually slightly better than that of the seed.

Agitation

To have a regular and even growth, the level of supersaturation has to be maintained equally around the surface of the growing crystal. An uneven growth leads to localized stresses at the surface generating imperfection in the bulk crystals. The concentration gradients that exist in the growth vessels at different faces of the crystal also cause fluctuations in supersaturation, seriously affecting the growth rate of individual faces. The gradient at the bottom of the growth vessel exceeds the metastable zone width, resulting in spurious nucleation. The degree of formation of concentration gradients around the crystal depends on the efficiency of agitation of the solution. This is achieved by agitating the saturated solution in either direction at an optimized speed using a stirrer motor.

Crystal habit

The growth of a crystal at approximately equivalent rates along all the directions is a prerequisite for its accurate characterization. This will result in a large bulk crystal from which samples of any desired orientation can be cut. Further, such large crystals should also be devoid of dislocation and other defects. These imperfections become isolated into defective regions surrounded by large volumes of high perfection, when the crystal grows with a bulk habit. In the crystals which grow as needles or plates, the growth dislocations propagate along the principal growth directions and the crystals remain imperfect. Needle like crystals have very limited applications and plate like crystals need to be favourably oriented. Changes of habit in such crystals which naturally grow as needles or plates can be achieved by any one of the following ways: (i) Changing the temperature of growth, (ii) Changing the pH of the solution, (iii) Adding a habit modifying agent and (iv) Changing the solvent.

Nonlinear Optical Phenomenon

Nonlinear optics is completely, a new effect in which light of one wavelength is transformed to light of another wavelength. The creation of light of new wavelength can be understood, only if the nature of the electrons in nonlinear optical crystal is studied. Electrons in a nonlinear crystal are bound in potential well, which acts like a spring, holding the electrons to lattice point in the crystal. If an external force pulls an electron away from its equilibrium position, the spring pulls it back with a force proportional to the displacement. The springs‟ restoring force increases linearly with the electron displacement from its equilibrium position. The electric field in a light wave passing through the crystal exerts a force on the electrons and pulls them away from their equilibrium position. In an ordinary optical material, the electrons oscillate about their equilibrium position at the frequency of this electronic field. According to the fundamental law of physics, an oscillating charge will radiate at its frequency of oscillation, hence these electrons in the crystal "generate" light at the frequency of the original light wave.

Theoretical Explanation of Nonlinear Optics

In a nonlinear medium, the induced polarization is a nonlinear function of the applied field. A medium exhibiting SHG is a crystal composed of molecules with asymmetric charge distributions arranged in the crystal in such a way that a polar orientation is maintained throughout the crystal.

Nonlinear Optical Materials

Advances in the development of NLO materials can be divided into three different areas.

- Discovery of new NLO materials
- Growth of promising NLO crystals
- Improving the characteristics of NLO crystals

For an NLO crystal device to work well without degradation of its performance over the life time of its assignment, the following criteria are required to be fulfilled:

- Wide optical transparency domain
- Large nonlinear figure of merit for frequency conversion
- High laser damage threshold
- Ready availability in large single crystals, thin films, etc.
- Wide phase matchable angle
- Ease of fabrication
- Nontoxicity and good environmental stability
- High mechanical strength and thermal stability and
- Fast optical response time.

Conclusion:

The growth and characterization of NLO single crystals are critical for the development of various applications that rely on the strong nonlinear optical properties of these materials. The growth process and characterization techniques used are dependent on the specific properties and requirements of the NLO single crystal under investigation.

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