Synopsis

"Investigations on the growth and characterisation of some technologically important single crystals for possible nonlinear optical applications"

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Introduction

In the modern world, the development of science & technology in many areas has been achieved through the growth of single crystals. Large sized single crystals are essential for device fabrication and efforts are taken to grow large single crystals in short duration with less cost.

The search for efficient and new materials in which to carry out investigations on non linear optical processes has been very active since the discovery of second harmonic generation (SHG) in quartz crystal by Franken and his co-workers in 1961.

Nonlinear optical (NLO) materials are expected to play a major role in photonics including optical information processing, sensor protector applications, data storage…etc. Some organic compounds exhibit large NLO response, in many cases, orders of magnitude larger than widely known inorganic materials. They also offer the flexibility of molecular design and the promise of virtually an unlimited number of crystalline structures. In this stimulating context, organic nonlinear materials have been recognized as forefront candidates for fundamental and applied investigations involving, in a joint effort, chemists, material scientists and optical engineering.

The database for nonlinear optical properties of materials, particularly organic, is in many cases inadequate for determining trends to guide synthesis efforts. Materials found in non-centrosymmetric, or acentric crystal classes, i.e. crystal classes lacking a center of inversion, can exhibit a variety of technologically important physical properties. Only a few molecules with large hyperpolarizability (γ) values crystallize in noncentrosymmetric structure, and a limited number of them are useful as NLO materials. There are crystals with large γ values and non centrosymmetry, but many of them do not have mechanical strength, thermal and air stability and perfection necessary for device fabrication.

Objectives of the present work

Amino acids, Glycine and L- Alanine and their complexes are bio compatible materials and are studied widely owing to their potential applications in the field of medicine. The chiral amino acid, L-Alanine is an efficient organic NLO compound under the amino acid category. They are formed as transparent crystals and are identified as systems with delocalised electrons. Delocalisation can be increased by reacting with carboxylic acids, thereby modifying the NLO behaviour. When glycine or l alanine is treated with oxalic acid the charge transfer complex formed due to the protonation of the amino group of the amino acid and the mono ionised oxalate ion in the crystal structure creates a donor- acceptor group resulting in intramolecular charge transfer which results in increased hyperpolarizability. Both glycinium oxalate (GLO) and L alaninium oxalate (LAO) are formed as noncentrosymmetric crystals.

Potassium hydrogen phthalate is a non centrosymmetric molecular ionic crystal. Potassium hydrogen phthalate crystals (KAP) are widely used in the field of X-ray spectroscopy as monochromator and also as analyser. It has interesting optical, piezoelectric and elastic properties. Recently, KAP crystals have been used as substrates for the deposition of thin films of organic nonlinear materials.

Studies on the growth and structural characterisation of all the three materials mentioned above have already been carried out, but the NLO behaviour of these materials has not been dealt with in detail. In the present work, we concentrate on the NLO behaviour of these materials and try to establish a connection between their structure and the NLO behaviour. Growth of large sized and optically perfect L-alaninium oxalate single crystals by solution growth technique and that of potassium hydrogen phthalate crystals using gel growth method are reported for the first time.

Brief outline of the work presented in the thesis

The thesis is divided into six sections. The first chapter is an introductory section on crystal growth and non linear optics. The second chapter deals with the relevant theoretical aspects of the present investigations. The details of the various experimental techniques employed in the present work are included in the third chapter. The fourth chapter gives an account of the growth of glycinium oxalate single crystals and their structural, thermal and nonlinear optical characterisations. In the fifth chapter detailed aspects of similar investigations on the other amino acid based charge transfer complex, L alaninium oxalate single crystals are included. The details of the growth of potassium hydrogen phthalate also known as potassium acid phthalate (KAP) single crystals by floating seed technique and also by sodium meta silicate gel growth method are included in chapter six. This chapter also gives an account of the various charecterisation techniques employed to evaluate the prospects of this material for NLO applications. The seventh chapter gives a summary of the important outcomes of the present investigations. It also gives a comparative assessment on the prospects of the three single crystals investigated in the present work, glycinium oxalate, and l- alaninium oxalate and potassium hydrogen phthalate, for possible non linear optical applications. The scope for future investigations on these materials is also highlighted in this chapter.

In the present study we have employed the characterisation tools such as Powder XRD, CHN analysis, EDAX, FTIR, FT Raman, UV/Vis/NIR spectroscopy, SEM, Optical microscopy , Vickers' microhardness analysis, Microtopography and chemical etching studies to reveal the growth mechanism and to determine dislocation density, TGA / DTA, Differential scanning calorimetry , Photoluminescence, Microwave dielectric studies using cavity perturbation method, Second Harmonic Generation(SHG) studies, Laser damage threshold studies and Third order Nonlinear Optical studies by Z scan method, under Open Aperture(OA) and Closed Aperture(CA) configurations.

Glycinium oxalate single crystals are grown from the saturated solution at ambient temperature using the precursors γ glycine and oxalic acid. An aqueous solution of 1:1 molar ratio glycine and oxalic acid maintained at 60^0C yields a white crystalline powder which is then recrystallized several times to get ultrapure glycinium oxalate. It is then used for the preparation of seed crystals and for making saturated solution for the growth of large sized single crystals. Powder XRD study on the grown crystal agrees well with the reported single crystal XRD data. CHN analysis confirms the molecular formula as $C_4H_7NO_2$. The vibrational analysis carried out using the FTIR and FT Raman spectroscopy shows the presence of NH_3^+ ion confirming the protonation of amino group leading to the formation of glycinium oxalate molecule. The non centrosymmetry in the grown crystals of glycinium oxalate is established on the basis of the excellent match between the various vibrational frequencies in the Infrared and Raman spectra.

Thermal studies carried out employing TGA/DTA and DSC techniques, establish that the crystal has thermal stability up to 180^0C (Melting point) and there is no phase transition till the material melts. The specific heat Cp, evaluated using the DSC data, is 898 J/kg Kat 333k. This relatively high Cp value enhances its prospects of applications in laser assisted devices. Vickers' microhardness analysis carried out on the material suggests that the material belongs to soft material category. The value of load independent resistance to deformation is calculated as 19.2 g. The value of elastic stiffness coefficient C_{11} calculated is quite high, revealing the strong binding force between ions. Microtopography and chemical etching studies are carried out to understand the growth mechanism and the nature and density of dislocations present in the crystal. Dislocation density for solution grown GLO, in the present study is about $10^4/cm^2$ which is quite small compared to many other solution grown inorganic semiconductors. It is established that growth mechanism of GLO single crystals in the present work is 2D nucleation and subsequent spreading of layers.

From the optical absorption studies in the UV/Vis/NIR range, it is seen that the GLO crystal has a wide transparency window ranging from 324 nm to 2500nm and the absorption throughout this range is very small. This aspect highlights its prospects of applications as a material for higher harmonic generation in nonlinear optics. The optical band gap of the material is found to be 3.9 eV. The value of the linear optical constants, α, n and k are evaluated and these values are used to compute the non linear optical parameters from the Z scan studies.

The value of dielectric constant at the microwave frequency in the S band is calculated as 3.3 for GLO crystals and it remains almost constant with increase in frequency in the frequency range 2-3 GHz. The value of dielectric loss for this crystal is very small which is of the order of 0.010, and is an indication of the crystalline perfection of the grown crystal.

The photoluminescence spectrum obtained, on exciting with 260nm radiation shows an emission peak at 470 nm which is assigned to a lattice related de excitation process from the LUMO to HOMO. This intense emission peak at 470 nm observed in GLO crystal extends ample scope for further detailed investigations in this direction.

Kurtz & Perry Powder technique is employed to investigate the second harmonic generation (SHG) process in this crystal. The SHG efficiency of the crystal is found to be 0.92 times that of KDP.

The single shot (P_1) and multiple shot (P_n) laser damage threshold values for (010) cleaved face of GLO are found to be 15.5 and 11.5GW cm^{-2}, respectively for 1064 nm, pulsed Nd: YAG laser radiation. Open aperture Z scan studies carried out using 532nm radiation of the pulsed Nd: YAG laser of 7ns pulse width, shows that there is reverse saturable absorption (RSA) in the material and two photon absorption is the mechanism responsible for RSA. The peak-valley structure of the curve obtained in the closed aperture Z scan studies is a clear indication of a negative nonlinear refraction exhibited by the crystal. The nonlinear refraction coefficient n_2 (m^2/W), hyperpolarizability (γ) and the real and imaginary parts of $\chi^{(3)}$ are evaluated. The ratio of the imaginary part of third order susceptibility to its real part is less than 1/3 which indicates that the observed non linearity in this crystal is electronic origin.

In the present work, top seeded solution growth technique at ambient temperature yields optical quality crystals of l- alaninium oxalate (LAO) of size 40 mm×30mm×10mm in three weeks time which is reported for the first time. As before the chemical composition of LAO is confirmed on the basis of CHN analysis and the crystal structure, by XRD analysis. The protonation of the amino acid group leading to the formation of LAO molecule is confirmed based on FTIR and Raman studies. Here also the excellent match between the various vibrational frequencies in the infrared and Raman data confirms that the grown LAO crystal is non centrosymmetric. The thermal studies on LAO crystal using TGA/DTA and DSC techniques show that the material is stable up to its melting point of 196 ^{0}C which is higher than that of GLO crystal. The value of Cp calculated from the DSC data is also greater than that of GLO. As before, from the micro hardness studies, the strong binding nature of ions in the crystal is established, which is an indication of its stability. Dislocation density evaluated for LAO crystal on the basis of etching studies is of the order of10^3 /cm^2 which is an order of magnitude less than that of GLO. The growth mechanism in LAO crystal is identified as 2D nucleation and subsequent spreading of layers.

In this material, from the optical absorption studies, the transparency window is found to extend from 318 nm to 1700nm and the optical band gap estimated is around 4.01 eV. As before the linear optical constants n, k and α are determined.

PL spectrum shows a broad peak centered at 440 nm with intensity comparable to that of conducting polymers and polymer composites when excited with 300nm radiation, which is also assigned to a lattice related LUMO to HOMO de excitation process. The very low value of dielectric loss obtained from the microwave absorption studies shows the good crystalline perfection of the grown LAO crystal.

SHG efficiency evaluated as explained before is 1.8 times that of L alanine and 2.3 times that of KDP. For the (100) plane, the single shot laser damage threshold P1 = 29.64 GW/cm^2 and multi shot damage threshold Pn = 22.60 GW/cm^2 and these values are much higher compared to GLO. Reverse saturable absorption (RSA) due to two photon absorption is confirmed from the open aperture Z scan method. Negative nonlinear refraction present in the material is observed in closed aperture Z scan experiment. As before the various nonlinear optical parameters are evaluated for this material also.

In the growth of potassium hydrogen phthalate (KAP) single crystals both floating seed technique and gel growth method are employed. In floating seed technique, the seed crystal placed on the saturated solution remains on the surface by surface tension and grows by evaporation of the solution. In three weeks time hexagonal crystals without any inclusions and defects with size 12 mm×10mm×5 mm are obtained.

Solubility reduction method employing sodium meta silicate gel is also tried for the growth of KAP crystals. A PH value of 5 is maintained for the gel and 3 molar KAP solution is added to the gel. A mixture of ethyl alcohol and acetone is poured over the gel and it is seen that in about one month, crystals of size l 0 mm× 4mm × 3mm are grown.

CHN analysis and EDAX are used to confirm the formation of potassium hydrogen phthalate. Powder XRD data of the solution grown and gel grown KAP crystal matches very well with the reported values. Excellent thermal stability up to 298^0C (melting point) is observed In KAP crystal without any phase transition. The Cp value at 333K is 860 J/kg K, which is quite high. Vickers' microhardness analysis shows that KAP belongs to the soft material category and is a stable material owing to the strong binding forces between the ions.

Layer growth is seen to be the prominent growth mechanism in the crystals grown by floating seed technique and also by gel growth method. Dislocation density is small ($10^3/cm^2$) and comparable to GLO and LAO. The crystal has a wide transparency window from 313nm to 1800 nm. Optical band gap is found to be 4.1ev. The linear optical constants are also determined. The low dielectric loss found in the material by cavity perturbation technique underlines the crystalline perfection.

SHG efficiency is found to be 2.5 times that of KDP for solution grown crystals and 3.1 times that of KDP for gel grown crystals. Gel grown KAP crystal shows enhanced SHG output owing to the better crystalline perfection with lesser defects, which is a positive aspect of the gel growth technique.

The value of single shot laser damage threshold is 25 GW/cm^2 and that of multiple shot laser damage threshold 19.6 GW/cm^2. The optical limiting and the non linear refraction in this crystal are established based on open aperture and closed aperture Z scan studies , similar to GLO and LAO crystals, and the various nonlinear optical parameters are evaluated.

A comparative analysis of the various important parameters of the three grown crystals, GLO, LAO and KAP is carried out for their possible applications in nonlinear optics.

The results of the present investigations allow ample scope for further investigations in these single crystals as outlined below

- Studies on the prospects of GLO and LAO crystals as bio compatible capping agents for ZnS and ZnO nano particles for bio medical imaging and targeted drug delivery applications can be carried out.
- Other growth methods like melt growth can be employed to get still bigger crystals of GLO, LAO and KAP for possible industrial applications.
- Suitable dopants can be incorporated to modify the NLO behaviour of these crystals.
- Microwave absorption studies can be extended to the whole micro wave region.

List of Publications

In peer reviewed international journals

1. Growth and characterization of glycinium oxalate crystals for nonlinear optical applications, **Arun.K.J**, S.Jayalekshmi, ***J. Optoelectron. Adv. Mater (RC)***, ***Vol.2, No.11, p701-706, (2008).***

2. Studies on the microstructure and micro hardness of L-alaninium oxalate single crystals for optical devices, **Arun.K.J**, S.Jayalekshmi, ***J. Optoelectron. Adv .Mater (RC), Vol.2, No.12, p802-805, (2008).***

3. Studies on the vibrational spectra of the nonlinear optical crystal L-alaninium oxalate, **Arun.K.J**, S.Jayalekshmi, ***AIP Conf .Proc. 1075, 115-117,(2008)***

4. Growth and charecterisation of nonlinear optical single crystals of L-alaninium oxalate, **Arun.K.J**, S.Jayalekshmi
   Journal of Minerals and Materials Charecterisation & Engineering, **U.S.A (**Accepted).

Conference Presentations

1. L-Alanium Oxalate single crystals for NLO applications: A simple and novel synthesis route, **Arun. K.J**, S. Jayalakshmi, ***Proceedings of the International conference on Optoelectronic Materials and Thin films***, October 24-27, 2005 Cochin University.

2. Growth and characterization of a new amino acid based mixed crystal for possible NLO applications, **Arun. K. J**, S. Jayalakshmi, M.A. Ittyachan, ***Proceedings of the National conference on Advanced technologically Important crystals***, October 12- 14, 2006, University of Delhi

3. Micro topography and micro hardness of L alaninium oxalate crystal, **Arun.K.J**, S.Jayalekshmi, ***Proceedings of the national conference- New horizons in theoretical and experimental physics,*** CUSAT, 2007.

4. A novel nonlinear optical mixed crystal Bis thiourea Potassium acid phthalate, **Arun. K. J**, S. Jayalekshmi, ***Proceedings of the national conference on current trends in materials science***, March 25-27, 2007, Christian college, Chengannur, Kerala

5. Studies on the Vibrational Spectra of the Nonlinear Optical Crystal L – Alaninium oxalate, **Arun.K.J**, S. Jayalakshmi, ***Proceedings of the International conference on perspectives in vibrational spectroscopy***, February 2008, Kerala University.

6. Microtopography, Microhardness and Vibrational Spectroscopic Studies on the Nonlinear Optical Crystal: Glycinium Oxalate, **Arun.K.J**, S.Jayalekshmi, ***Proceedings of the International conference on perspectives in vibrational spectroscopy***, February 2008, Kerala University.