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Growth and Characterization of Guanidinium based Organic and Semi-Organic Single Crystals for Nonlinear Optical Applications

A. Suvitha[1], P. Murugakoothan*

[1]Department of Physics, Anna Adarsh College for Women, Chennai - 600 040, India.
*MRDL, PG and Research Department of Physics, Pachaiyappa's College, Chennai - 600 030, India.

Guanidinium complexes arebiologically important as they are present as functional groups in aminoacids. Their physical properties, are so important that they have a variety of applications in the field of ferroelectricity, biotechnology medicine etc. The present work deals about the growth and characterization of guanidinium 3-nitrobenzoate (Gu-3NB), guanidiniumphenylarsonate (GPA), zinc guanidinium phosphate (ZGuP) and guanidiniumchlorochromate (GCC). Structural analysis, linear and non-linear optical properties, Laser damage threshold and thermal stability of the grown crystals have been investigated to check their viability for non-linear optical applications.

Introduction

Crystal growth plays an important role in basic researches related to laser technology, optical communication and optical data storage. The improvement in laser technology and discovery of new organic and inorganic non-linear optical materials over the recent years have contributed significantly to the field of non-linear optics. The semi-organic compounds share the properties of both organic and Inorganic compounds. They are organic based materials in which the polarizable part is an organic molecule which is stoichiometrically bonded with an inorganic ion. The metal-organic crystals form a new class of materials under semi-organics. Compared to organic molecules, metal complexes offer a large variety of structures, and a diversity of electronic properties by virtue of the coordinated metal centre. Guanidinium complexes play a vital role in the field of non-linear optics. Guanidine is a strong Lewis base (pKa 13.5) and readily reacts with all types of organic acids to give salts with good crystallinity. The presence of six potential donor sites for hydrogen-bonding interactions and delocalized electron systems has made guanidine compounds potentially interesting material for nonlinear optical applications [1]. The present work deals with the growth and characterization of some organic, semiorganic and metal-organic nonlinear optical crystals, such as guanidinium 3-nitrobenzoate (Gu-3NB), guanidiniumphenylarsonate (GPA), zinc guanidinium phosphate (ZGuP) and guanidiniumchlorochromate (GCC).

Corresponding: suvi.arumugam@gmail.com

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2. Synthesis and Crystal Growth

Compounds of guanidine with 3-nitrobenzoic acid, phenylarsonic acid, orthophosphoric acid and chromium trioxide yielded good quality crystals namely Gu-3NB, GPA,,ZGuP and GCC. All the above-mentioned compounds are synthesized by slow evaporation technique in different solvents at room temperature. The grown seed crystals are shown in figure 1.1(a). The bulk crystals are grown by slow cooling technique in a constant temperature bath controlled with an accuracy of ± 0.01 ºC. The crystals and their morphology are shown in figure 1.1(b). The solubility of these compounds was determined for various solvents at different temperatures. It was found that their solubility increases linearly with temperature. The solubility of guanidinium compounds for various solvents are depicted in figures 2.1.

3. Results and Discussions

3.1 Single Crystal X-Ray Diffraction

Single crystal X-ray diffraction (SXRD) analysis is carried out in order to confirm the crystalline nature and lattice parameters of the grown crystals. The data obtained from the SXRD study is found to agree with the literature values. The observed structural data are given in Table 1.

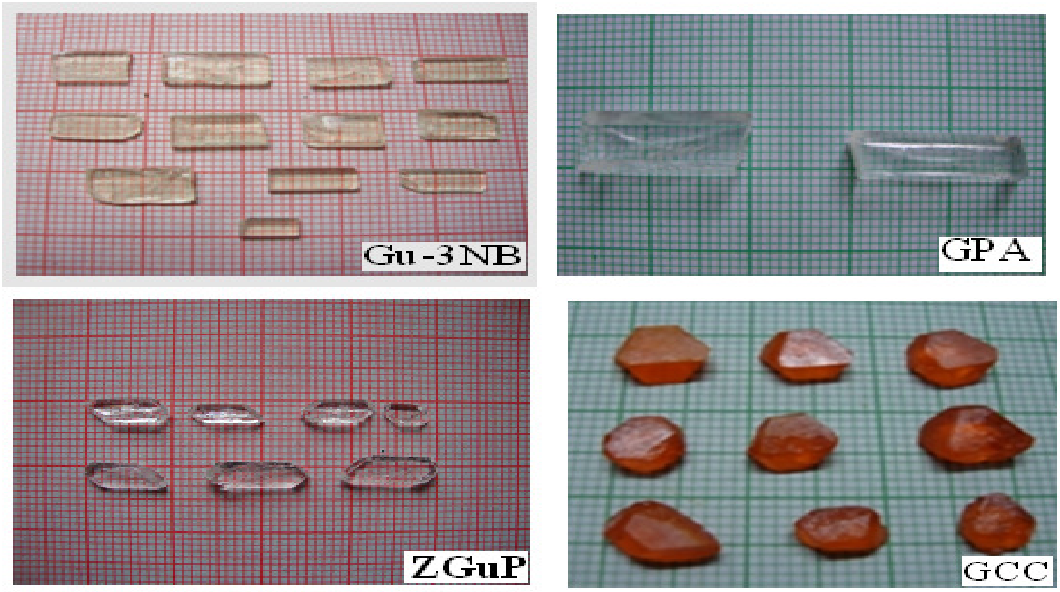


Fig. 1.1(a) Seed crystals of Gu-3NB, GPA, ZGuP and GCC grown by slow evaporation technique

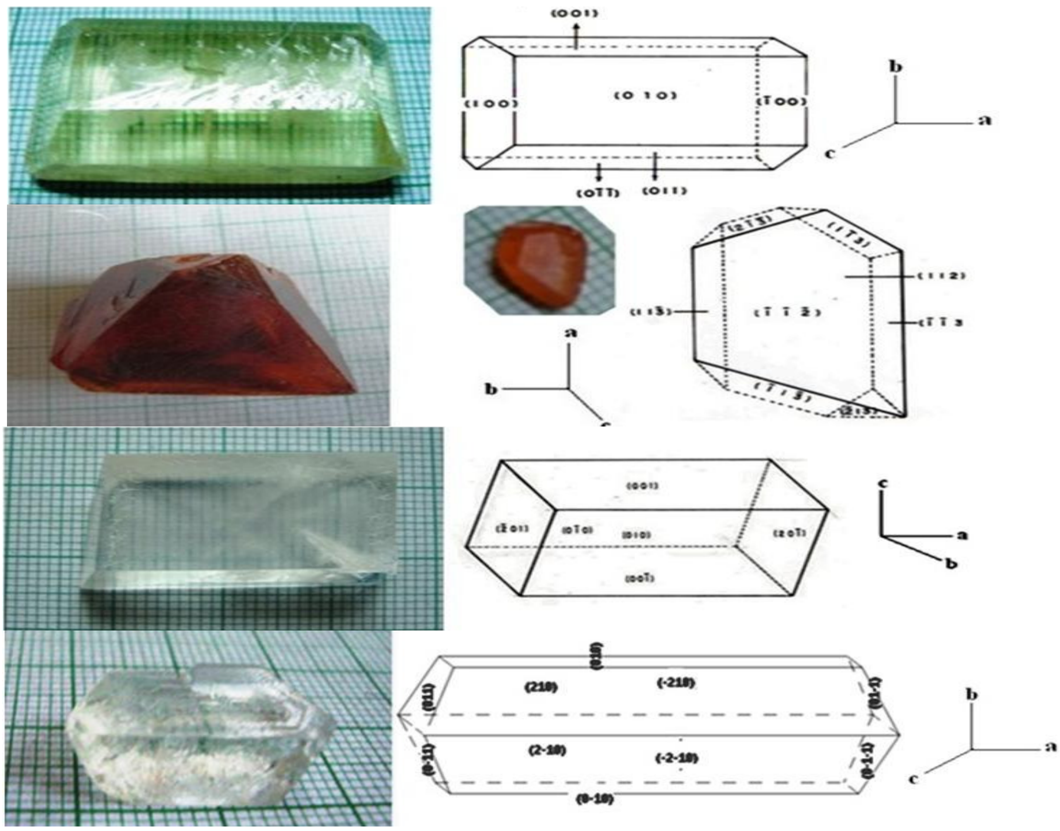


Fig. 1.1(b) Bulk crystals of Gu-3NB, GPA, ZGuP and GCC grown by slow cooling technique with Morphology.

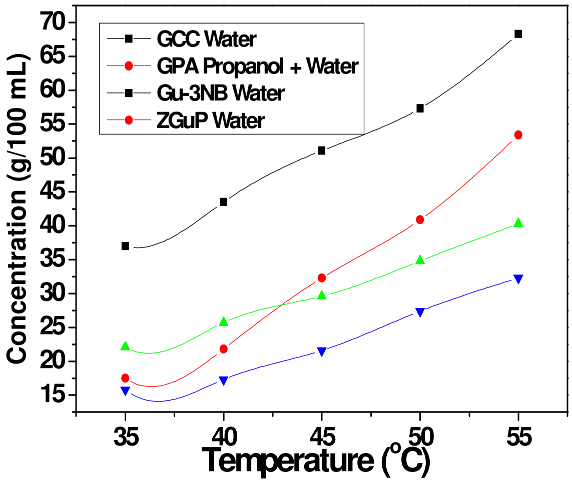


Fig. 2.1 Solubility curve of Gu-3NB,ZGuP, GCC and GPA

Crystal	Unit Cell Parameters	Space Group
Gu-3NB	a = 7.358 Å b = 10.091 Å c = 13.630 Å V = 1012.1 Å^3	Orthorhombic *P*2$_1$2$_1$2$_1$[5]
GPA	a = 18.453 Å b = 7.609 Å c = 12.592 Å β = 121.856° V = 1589.0 Å^3	Monoclinic Cc [6]
ZGuP	a = 5.124 Å b = 7.826 Å c =16.473 Å β= 90.117° V= 662.3 Å^3	Monoclinic *P*2$_1$[7]
GCC	a = 6.113 Å b = 7.540 Å c = 14.898 Å V = 685.3 Å^3	Orthorhombic *Pnma* [8]

Table 1. The single crystal XRD data for the grown crystals

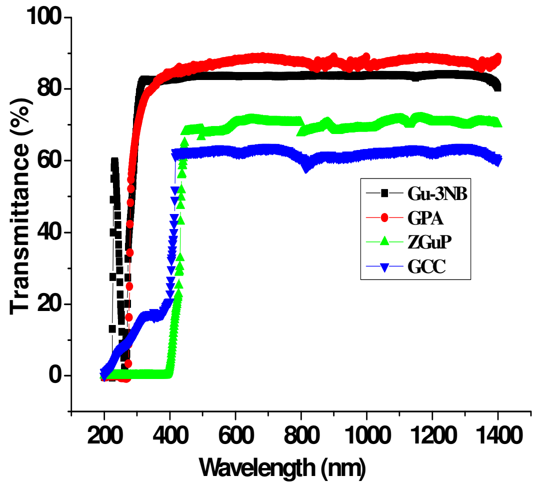
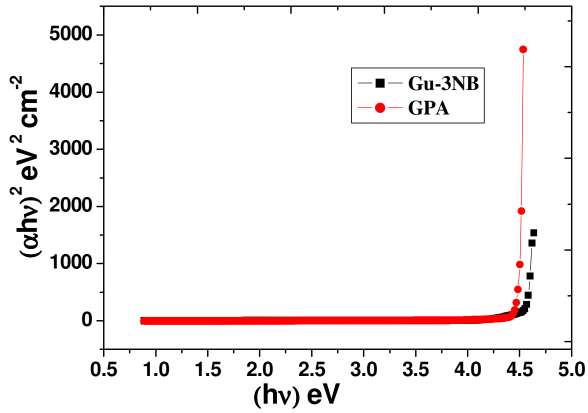


Fig. 3.1Transmittance spectra of grown crystals



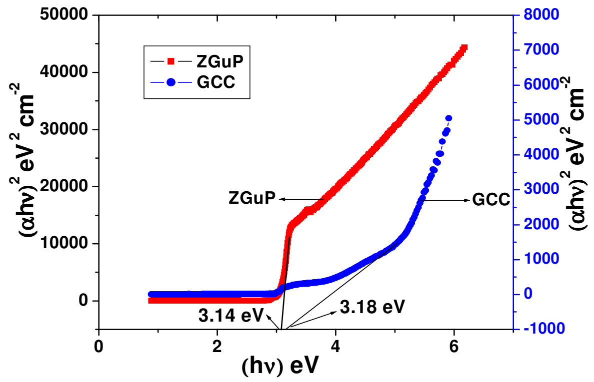


Fig. 3.2 plot of (αhν)^{2}vshν for grown crystals

3.2 UV – VISIBLE OPTICAL ABSORPTION STUDIES

The transmission range of the as grown guanidinium crystals, was determined by recording the optical transmission spectrum for the wavelength range 200 to 1400 nm. The crystals of thickness 2 mm were used for this measurement. The percentage of transmittance for Gu-3NB, GPA and ZGuP crystals, was found to be around 80% and 65% for GCC with lower cut-off wavelength at 265, 271, 395 and 390 nm respectively as shown in figure 3.1. From the spectra it was found that these crystals absorb UV radiation. Hence these crystals can also be used as an effective UV shelter [2]. From the Tauc's plot between $(\alpha h\nu)^2$ and photon energy $(h\nu)$ [3], the optical band gap value for the grown crystals, as shown in figure 3.2 was found to be 4.58, 4.49, 3.14 and 3.18 eV respectively.

3.3 NONLINEAR OPTICAL STUDY

The second harmonic generation efficiency of the as-grown guanidinium based crystals was studied by Kurtz powder test [4]. A fundamental beam from Q-switched Nd: YAG laser was passed through the powder sample of the grown crystals. The output of the laser beam showed a bright green emission (λ = 532 nm) from the powder sample. This confirmed the SHG behavior of the crystals. All the grown crystals have comparable value of SHG efficiency with that of potassium dihydrogen phosphate (KDP). The second harmonic generation efficiency of grown guanidinium series of crystals are listed in Table 2.

Crystals	SHG efficiency
KDP	1
Gu-3NB	0.438
GPA	0.785
ZGuP	1.825
GCC	0.483

Table 2. SHG efficiency of the grown crystals with respect to KDP

3.4 LASER DAMAGE THRESHOLD STUDY

The utility of NLO crystal depends not only on the linear and nonlinear optical properties but also on its ability to withstand high power lasers. Hence, the subject of Laser Damage Threshold (LDT) is of great importance to the design and successful operation of nonlinear devices. In the present work, an actively Q-switched Nd: YAG laser in TEM_{00} mode with pulse width 10 ns and repetition rate 10 Hz was used for the laser induced damage threshold studies.The focal point of the convex lens, which was used to focus the laser beam, was 30 cm and thickness of the samples range from 2mm-3mm were used in LDT measurement.The laser damage threshold study confirms that the grown crystals Gu-3NB and GPA exhibit higher LDT when compared with urea and KDP and is shown in Table 3.

Crystal	LDT (GW/cm^2)
KDP	0.20 [9]
Urea	1.50
Gu-3NB	3.84
GPA	4.08
ZGuP	2.6
GCC	3.06

Table 3. LDT values of Gu-3NB and GPA crystals

3.4 THERMAL ANALYSIS

Thermal stability is an important parameter for the crystals used for device applications. In the present study, the thermal characteristic of the grown Gu-3NB and GPA crystals were studied by TG-DTA technique between 30 °C and 800 °C at a heating rate of 2 °C/min. in the nitrogen atmosphere using NETZSCH STA 449F3.The TG - DTA of ZGuP is carried out between 28 ºC and 1000ºC and for GCC between 28 ºC and 1200ºC at a heating rate of 10 ºC min^{-1} using ZETZSCH – GeretebauGmbh Thermal analyser. Alumina crucible was used for TG-DTA thermal analyzer. The decomposition of the compounds Gu-3NB, ZGuP and GCC starts at 250 °C, 227°C and 163.5°Crespectively. The melting point of GPA was found to be 186.8 °C.The TG – DTA thermogram of the grown crystals is shown in figures 3.3 and 3.4. In order to have an idea about the thermal stability of the compounds grown in the present study, the initial mass-loss temperatures of these compounds are compared with some of the reported compounds in Table 3. From the comparison, it is clear that the grown guanidinium compounds are showing better thermal stability than some of the reported samples

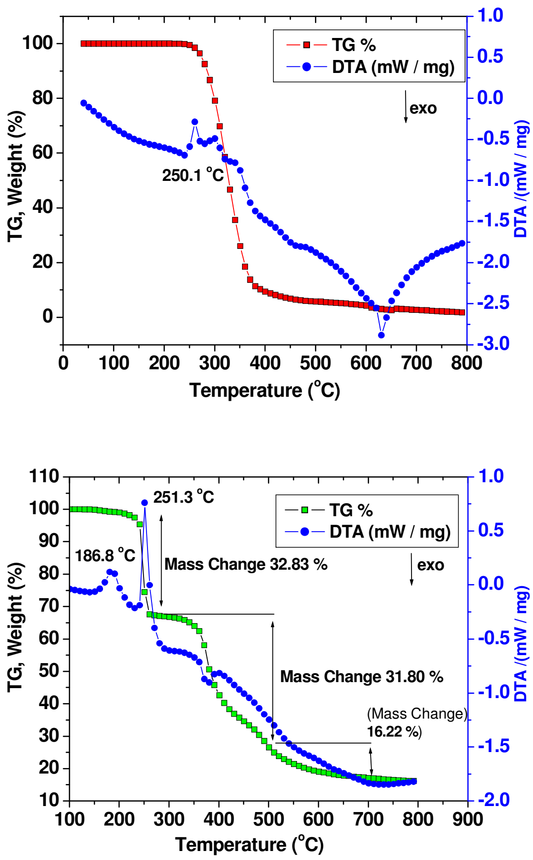


Fig. 3.3 TG-DTA thermogram of Gu-3NB and GPA

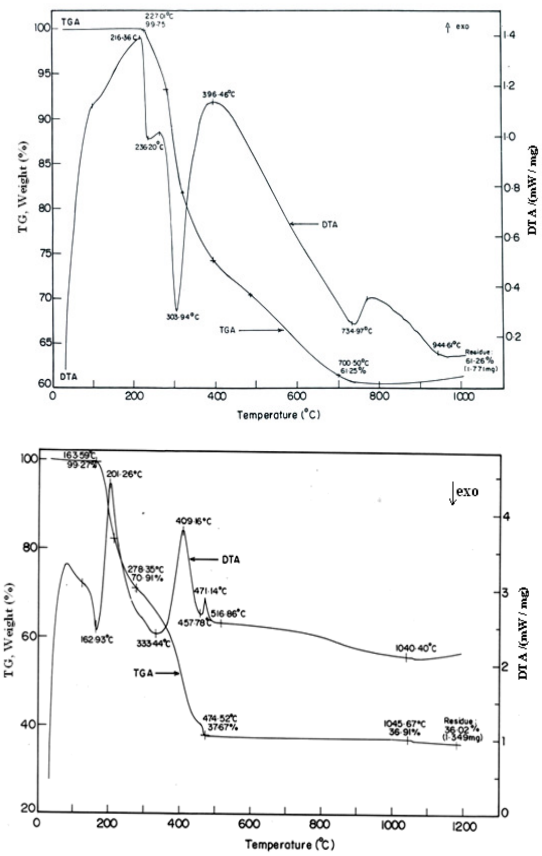


Fig. 3.4 TG-DTA thermogram of ZGuP and GCC

Crystals	Mass loss temperature (°C)
Guanidinium carbonate	190[a]
Guanidinium chloride	185[a]
Guanidinium acetate	200[a]
Guanidinium nitrate	215*[a]
Guanidinium L-monohydrogen tartrate (GuHT)	182
Guanidinium L-glutamate (GuGL)	205
Guanidinium3-nitrobenzoate (Gu-3NB)	250
GuanidiniumPhenylarsonate(GPA)	231
Zinc GuanidiniumPhosphate (ZGuP)	227
GuanidiniumChlorochromate(GCC)	163.5

Table 3. Initial mass-loss temperature for some uanidinium based crystals.

* Gradual mass-loss starting at 50 °C for guanidiniumnitrate.

[a](Wendlandt et al., 1984).

4. CONCLUSION

Optically good quality single crystals of guanidinium 3-nitrobenzoate (Gu-3NB), guanidiniumphenylarsonate (GPA), zinc guanidinium phosphate (ZGuP) and guanidiniumchlorochromate (GCC) were grown by slow evaporation technique. The formation of the crystal is confirmed by single crystal XRD. The properties, such as excellent optical transparency, good second harmonic generation efficiency, high laser damage threshold and high thermal stability of the grown guanidinium based single crystals prove them to be the potential candidates for nonlinear optical an d optoelectronics device fabrication

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