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Synthesis, growth, structural, optical and thermal properties of a new semiorganic nonlinear optical guanidinium perchlorate single crystal

V. Sivashankar[a,*], R. Siddheswaran[b], P. Murugakoothan[c]

[a] *Department of Physics, Kongu Engineering College, Erode 638 052, India*
[b] *Department of Materials Engineering, University of Concepcion, Concepcion-4070409, Chile*
[c] *Post Graduate & Research Department of Physics, Pachaiyappa's College, Chennai 600 030, India*

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ABSTRACT

The guanidinium perchlorate crystals were grown from aqueous solution by low temperature solution growth technique. The cell parameter values were found out using X-ray diffraction analysis. The presence of chlorine in guanidine perchlorate was estimated qualitatively by FTIR analysis. The optical transmittance window and the lower cutoff wavelength have been identified by UV–vis–NIR spectral analysis. Second harmonic generation efficiency is found to be 1.5 times that of KDP. Thermal stability of the crystal was investigated using thermo-gravimetric analysis. Microhardness studies were carried out using Leitz–Wetzler hardness tester at room temperature.

1. Introduction

The last few decades have witnessed a spectacular growth of multidisciplinary research activity involving materials that exhibit nonlinear optical (NLO) behavior. There has been a growing interest in the search for materials with large second-order nonlinearities because of their practical utility as frequency doublers, frequency converters and electro-optic modulators by means of second-harmonic generation, parametric frequency conversion (or mixing) and the electro-optic (EO) effect [1–4]. In order to optimize these effects, efficient NLO materials have to be engineered. Initially NLO activity was first found in semiconductors then in inorganic crystals [2,3] and followed by organic materials [5–9]. In particular, semi-organic systems provide many interesting structure and bonding schemes for the molecular engineering of highly efficient new NLO materials. In the present investigation guanidinium perchlorate (GPCl) has been chosen as potential material for non-linear optics. The guanidinium ion $C(NH_2)_3^+$ is a relatively simple chemical species whose structure is related to those of amides and proteins in which there is considerable current interest [10]. The guanidinium ion can form a broad family of hydrogen-bonded crystals. Guanidinium, besides its easy availability, has a number of advantages that make it an obvious molecular candidate as NLO material. Initially, the cation conformation supported by many X-ray crystal structure investigations reveal three equivalent C–N bond lengths of 1.325 Å and N–C–N bond angles of 120° indicating perfect threefold symmetry (D3h) [11]. The short C–N bonds exhibit a pronounced electron-acceptor π-bond character while NH_2 is a classical donor group. Guanidinium thus appears as a polarizable acentric two-dimensional cation to be regarded as a planar octupolar (molecules with symmetry close to three-fold rotational) chemical entity [11]. The use of octupolar organic molecules and ions has already been exemplified in the engineering of quadratic nonlinear-optical materials [12–15]. Moreover from the chemical point of view, guanidine is a strong Lewis base and the guanidinium cation may be easily anchored onto numerous inorganic and organic anions and polyanions through hydrogen-bonding networks [11]. In this paper, a report on synthesis, crystal growth, structural, optical, thermal and mechanical properties of GPCl have been studied and presented.

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* Corresponding author. Tel.: +91 9940357870.
E-mail address: tvsivashankar@yahoo.co.in (V. Sivashankar).

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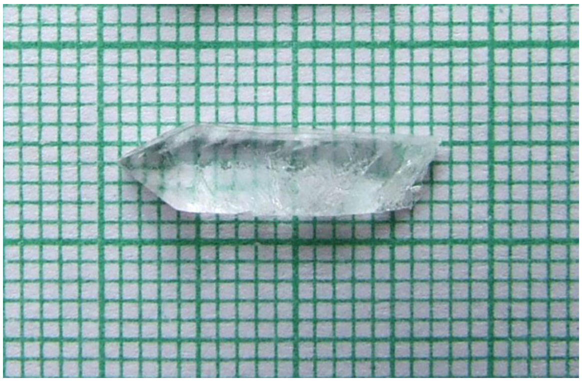

Fig. 1. GPCl single crystal.

2. Experimental procedure

2.1. Synthesis and crystal growth

The analytical reagent (AR) grade guanidinium carbonate and perchloric acid have been used for synthesizing. The starting material was synthesized in the stoichiometric 1:2 ratio by using the following reaction

$$[C(NH_2)_3]_2(CO_3) + 2HClO_4 \rightarrow 2[C(NH_2)_3ClO_4] + H_2O + CO_2$$

The calculated amounts of salts were dissolved in the deionized water. This solution was heated and kept for evaporation to dryness at room temperature. The purity of the synthesized salt was increased by successive recrystallization process. The purified GPCl salt was dissolved in deionized water and stirred continuously to obtain a homogenous solution. Optically good transparent crystals of size 16 mm × 5 mm × 3 mm were obtained by employing slow evaporation technique. The grown crystals are shown in Fig. 1.

2.2. Characterization

Single crystal X-ray diffraction analysis was carried out using an ENRAF-NONIUS-FR-590, CAD4, automatic X-ray diffractometer with MoKα radiation of wavelength, $\lambda = 0.717$ to determine the crystal structure and to estimate the lattice parameter values. Powder X-ray diffraction analysis was also carried out using a Rich Seifert diffractometer with CuKα ($\lambda = 1.5418$) radiation to verify the correctness of lattice parameter values with single crystal X-ray diffraction values and literature values. The chemical composition of the grown crystal was determined by carbon, hydrogen and nitrogen (CHN) analysis using the instrument Elementar Vario EL III-GERMANY analyzer. The FTIR spectra of GPCl crystals were recorded in the range 400–4000 cm^{-1} employing a Perkin-Elmer spectrometer by KBr pellet method in order to confirm the presence of functional groups. Linear optical properties of the crystal were studied using a Shimadzu UV-vis-NIR spectrophotometer. To confirm the nonlinear optical property, Kurtz powder SHG test was performed on the grown crystals. The thermal analysis was carried out using Perkin Elmer simultaneous thermogravimetry and differential thermal analysis (TG–DTA) analyzer to analyze the thermal stability of the compound. The Vickers's hardness measurement was carried out using a Leitz–Wetzler microhardness tester fitted with a Vicker's diamond pyramidal indentor on the grown crystals to assess the mechanical property.

3. Results and discussion

3.1. X-ray diffraction analysis

The crystal structure and lattice parameters of the crystal was examined by single-crystal X-ray diffraction analysis and the least square refinement of 25 reflections was done in the range 20–30°. The present study shows that guanidinium perchlorate crystallizes in the Trigonal system (space group R3m; hexagonal unit-cell dimensions $a = 7.605$ Å, $b = 7.605$ Å, $c = 9.121$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ and $Z = 3$). The grown single crystal of GPCl was subjected to powder X-ray diffraction. The sample was scanned over the range 10–60° at a scan rate of 2° min^{-1}. The recorded X ray pattern of GPCl is shown in Fig. 2. The indexed (h, k, l) planes satisfy the general reflection conditions of space group observed from the structure determination of the crystal. The experimental values were found to agree well with the calculated 'd' values.

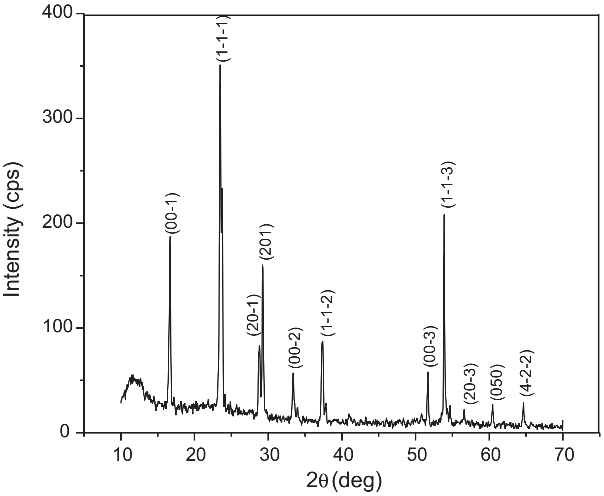

Fig. 2. X-ray powder diffraction pattern of GPCl.

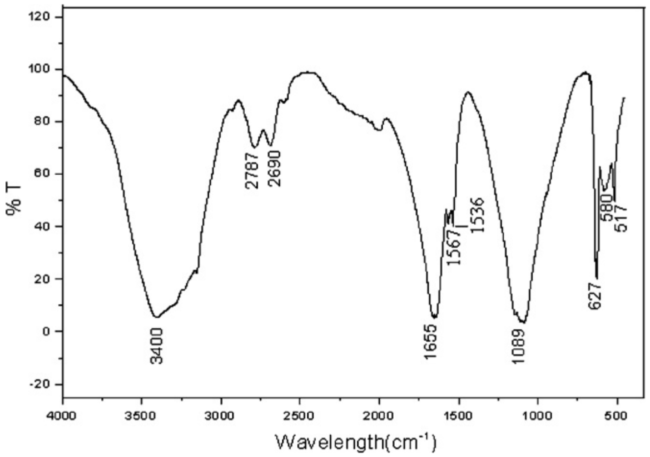

Fig. 3. FTIR spectrum of GPCl.

3.2. Chemical and Fourier transforms infrared (FTIR) analysis

In order to confirm the chemical composition of the synthesized compound CHN analysis was carried out on the grown sample and the results are shown in Table 1. The experimental results of CHN test shows that the percentage composition of C, H, N present in the synthesized material is in good agreement with that of calculated values of GPCl, thus confirming the molecular formula of the compound as $C(NH_2)_3ClO_4$.

Infrared spectroscopy has been used to identify the functional groups of the synthesized compound. The FTIR absorption spectrum of GPCl is shown in Fig. 3. The peak observed at about 3400 cm^{-1} is due to symmetric N–H···O stretching band. The peaks at 2787 and 2690 cm^{-1} are attributed to the O–H stretching mode vibrations. The intense sharp peak band at 1655 cm^{-1} is due to NH_2 inplane bending mode. The peak observed at about 1567 cm^{-1} is

Table 1
CHN analysis of GPCl single crystal.

Element	Composition (%)	
	Experimental	Theoretical
Carbon	7.70	7.52
Hydrogen	3.78	3.79
Nitrogen	26.84	26.34

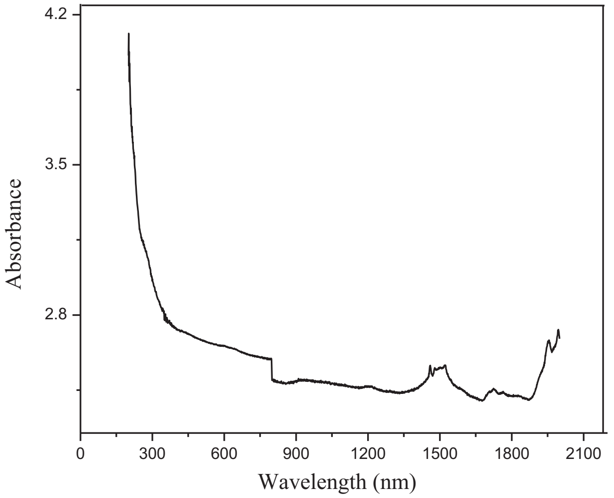

Fig. 4. UV–vis–NIR absorption spectrum of GPCl.

assigned for N–H bending character and the peak at 1536 cm^{-1} is due to C=N stretching. The sharp intense absorption at 1089 cm^{-1} can be assigned to the Cl–O stretching vibration. Hence the presence of perchlorate anion as the counter ion has been confirmed. A sharp band at 627 cm^{-1} indicates the rocking mode of NH_2. The bands at 580 and 517 cm^{-1} are assigned to symmetric CN_3 stretching.

3.3. Optical and non linear optical studies

An optical absorption spectrum was recorded in the wavelength range 200–2000 nm. A graph of absorbance versus wavelength ignoring the loss due to reflection is shown in Fig. 4. It is found that GPCl has a wide transmission window between 200 and 2000 nm with a transmittance of 75%. From the spectrum, it is noted that the UV transparency cutoff occurs at 250 nm, which is good enough for blue-violet light photonic applications. The optical band gap of the GPCl crystal is calculated using the formula

$$E_g = \frac{hc}{\lambda}$$

From the fundamental absorption at 250 nm the band gap energy of the material is found to be 4.9 eV.

The Kurtz powder second harmonic generation (SHG) measurements were carried out using high intensity Nd:YAG laser beam of wavelength 1064 nm with a pulse width of 10 ns at a repetition rate of 10 Hz [16]. The emission of green light from the GPCl samples confirmed the frequency doubling of the title crystal. The efficiency was found to be equal to 1.5 times that of standard KDP crystal. The SHG efficiency of GPCl crystal is compared with some standard semiorganic compounds and presented in Table 2.

Table 2
Comparative SHG efficiencies of various crystals relative to KDP.

Nonlinear optical crystals	SHG efficiency
GPCl	1.5
L-Arginine chloride	0.2
L-Arginine bromide	0.3
L-Tyrosine hydrobromide	1.2
L-Histidine bromide	1
L-Ornithine hydrochloride	0.52
L-Arginine perchlorate	3.12

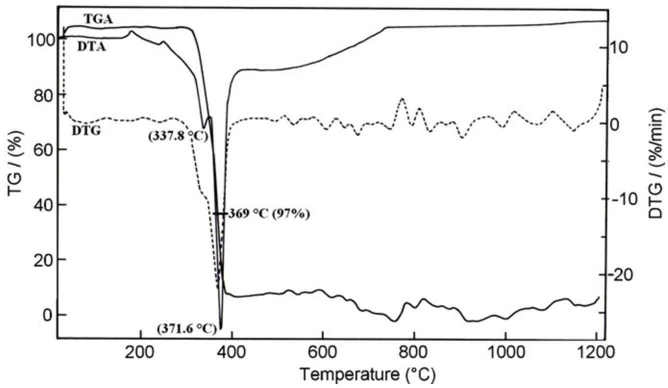

Fig. 5. TG–DTA curves of GPCl.

3.4. Thermal analysis

The TG–DTA curves for GPCL crystal are shown in Fig. 5. These curves were performed in an nitrogen atmosphere at a heating rate of 20 °C min^{-1}. From the TG–DTA curves it is inferred that the material starts decompose at about 337 °C. This confirms the absence of any water molecule in the crystal lattice. Further mass loss occurs in very small steps due to the release of volatile substances in the compound, probably ammonia and oxides of chlorine. TGA shows that a complete mass loss takes place at around 369 °C. From the DTA curve it is observed that the endothermic peak at 371.6 °C nearly trace the corresponding decompositions in the TGA. Prolonged heating up to 1200 °C does not produce any significant endothermic or exothermic peaks in the DTA curve. Hence, based on these analyses it can be ascertained that the maximum temperature below which the crystal can be exploited for application is 337 °C.

3.5. Dielectric studies

For dielectric measurements, carefully cut and polished samples of grown crystals were carried out using HIOKI 3532-50 LCR HITESTER in the frequency range 100 Hz–5 MHz. A sample of crystal having silver coating on the opposite faces was placed between the two copper electrodes to form a parallel plate capacitor. Fig. 6 shows the plot of dielectric constant (ε') versus applied frequency. From the graph, it can be shown that the dielectric constant decreases, indicating that the grown crystals possesses improved

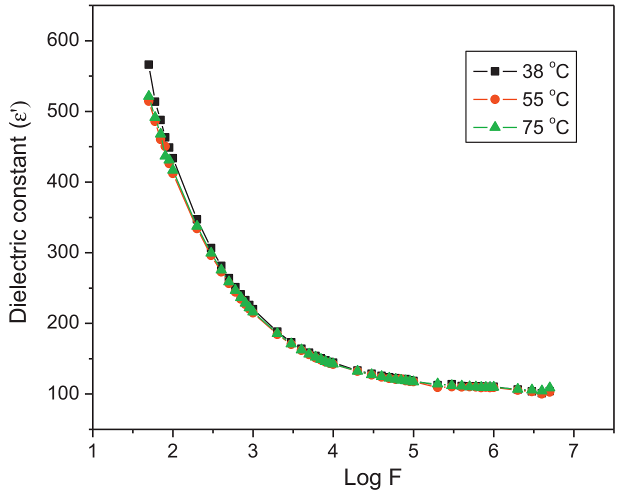

Fig. 6. Variation of dielectric constant with frequency of the applied electric field.

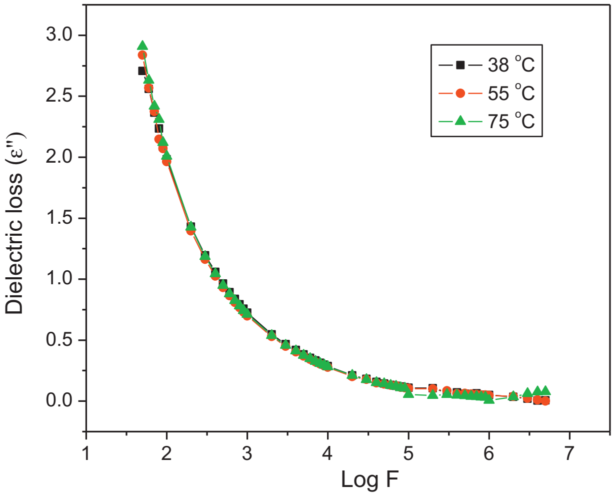

Fig. 7. Variation of dielectric loss with frequency of the applied electric field.

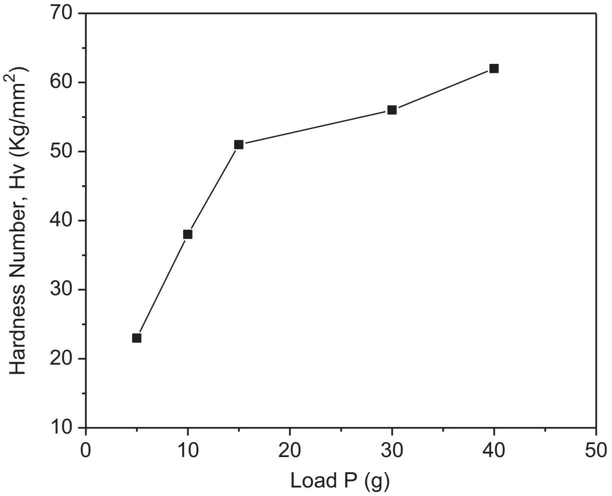

Fig. 8. Hardness number (Hv) versus load (*P*) of GPCl.

pyroelectric properties [17,18]. The very low value of dielectric constant at higher frequencies is important for the fabrication of materials towards ferroelectric, photonic and electro-optic devices. The dielectric loss, studied as a function of frequency at room temperature is shown in Fig. 7. The very low dielectric loss reveals the very high purity of the crystals. These curves suggest that dielectric loss is also strongly dependent on the frequency of the applied field.

3.6. Microhardness analysis

Microhardness measurement studies were carried out to analyze the mechanical strength of the titled compound. After the preliminary adjustments, well polished smooth surface (100 face) of the crystal was subjected for the analysis. Microhardness measurements were done for applied loads (*P*) varying from 5 to 50 g. The indentation time was maintained constant at 10 s. Several trials of indentations were made and the hardness values were calculated using the relation $Hv = 1.8544P/d^2$, where Hv is the Vickers hardness number in kg mm^{-2}, *P* is the indentor load in kg and *d* is the diagonal length of the impression in mm. The graph has been plotted against the Vickers hardness number (Hv) and load (*P*) and is shown in Fig. 8. From the graph it is clear that the Vickers hardness number increases with the increase of load. For loads above 40 g, cracks started developing around the indentation mark. This may be due to the release of internal stress generated locally by indentation. The hardness value measured for GPCl crystal at 40 g is 60.5 kg mm^{-2}.

4. Conclusion

The new nonlinear optical crystal guanidinium perchlorate was synthesized and single crystals of dimension up to 16 mm × 5 mm × 3 mm were grown by slow evaporation technique using water as solvent. Lattice parameter values were found using powder X-ray diffraction analyses. Elemental analysis confirms the formation of the title compound. Various functional groups present in GPCl were identified by FTIR spectrum. The GPCl crystal has good optical transparency in the entire visible region of electromagnetic spectrum. The powder SHG efficiency of GPCl was found to be 1.5 times that of standard KDP. The grown crystals were thermally stable upto 337 °C. Microhardness of the grown crystal was studied and the Vickers hardness number of GPCl was found to be 60.5 kg mm^{-2}. Owing to good thermal, mechanical and chemical stability, it is a promising candidate for NLO applications.

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