Current Applied Physics 14 (2014) 156–160

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Evidence of sustained ferroelectricity in glycine sodium nitrate single crystal

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A R T I C L E I N F O

Article history:
Received 27 July 2013
Received in revised form
29 October 2013
Accepted 4 November 2013
Available online 15 November 2013

Keywords:
Organo-metallic compound
Crystal growth
Thermal analysis
Dielectric properties
Ferroelectricity

A B S T R A C T

The nonlinear optical single crystals of glycine sodium nitrate were grown by the slow evaporation method. XRD confirmed monoclinic structure. Thermal stability and melting point (225 °C) were investigated. The dielectric behaviour of the crystals in the frequency range 20 Hz–2 MHz at different temperatures is reported in which a ferroelectric to paraelectric phase transition at T_c = 56 °C is observed. The activation energies of GSN were found to be 3.615 eV, 0.593 eV and 0.0733 eV in three temperature regions of conductivity plot due to a hopping conduction mechanism. The crystal has shown high piezoelectric charge coefficient (d_{33}) of 16 pC/N which is nearly double of observed value for γ-glycine single crystal. The spontaneous polarization P_s at room temperature was found to be 1.489 μC/cm^2 at applied maximum field of 26 kV/cm (1.194 μC/cm^2 at 12 kV/cm) and the pyroelectric coefficient was determined to be 400 μC/m^2/°C. High value of squareness parameter (1.93) makes the GSN crystal suitable for switching applications. Detailed investigations of Ferro-/Piezoelectricity were observed for the first time in glycine sodium nitrate crystals which was found to preserve the ferroelectricity even after applying an electric field much higher than the saturation electric field (12–26 kV/cm). Application of GSN crystals as sensor, high power switch gears and storage memories has been established.

1. Introduction

Amino acids are basic elements of biological materials. It has a proton donating carboxyl (COOH) group and a proton accepting amino (NH_2) group. Due to its chiral symmetry, amino acids are very useful for NLO applications and known to exhibit ferroelectricity, piezoelectricity and pyroelectricity [1,2]. Amino acid single crystals have low symmetry without inversion centre. Some complexes of amino acids are known to exhibit ferroelectric properties due to its polar symmetry group. Glycine is one of the simplest forms of amino acids and its various characteristic studies have been reported by many authors [3,4]. Many of glycine complexes have shown ferroelectricity such as Glycine silver nitrate [5], Glycine phosphate [6], Di-glycine manganous chloride dehydrates [7] etc. Due to important applications of ferroelectric materials in optoelectronics such as capacitors, nonvolatile memory devices, high-performance gate insulators etc, we attracted toward finding the material with have fairly good ferroelectric, piezoelectric and pyroelectric properties. Glycine sodium nitrate (GSN) is semi-organic NLO crystal having non-centrosymmetric structure and monoclinic crystal system with space group Cc. Its lattice constants with error are a = 14.4294 ± 0.0316 Å, b = 5.4095 ± 0.0034 Å, c = 9.1403 ± 0.0240 Å, $\alpha = 90°$, $\beta = 118.900° \pm 0.174°$ and $\gamma = 90°$ and Volume = 626.390 Å^3 [8]. Due to its polar symmetry system, there is possibility of ferroelectricity. Even though many reports are available on the nonlinear properties of glycine sodium nitrate crystals [9,10] but there is no report available on piezoelectric, ferroelectric and pyroelectric behaviour of these crystals. In the present work, single crystals of glycine sodium nitrate were grown and their structural, thermal, dielectric, piezoelectric, ferroelectric and pyroelectric properties have been reported.

2. Experimental

2.1. Synthesis and crystal growth

Glycine sodium nitrate (GSN) was synthesized by dissolving 1 mole of glycine and 1 mole of sodium nitrate in double distilled water. The reaction may be expressed as follows

$$C_2H_5NO_2 + Na\,(NO_3) \rightarrow Na\,(NO_3)\cdot C_2H_5NO_2$$

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http://dx.doi.org/10.1016/j.cap.2013.11.005

Crystal growth process was initiated with recrystallized GSN salt in a saturated solution at 35 °C which was kept in a constant temperature bath having an accuracy of ±0.1 °C. Controlled slow evaporation yielded crystals of size 12 mm × 10 mm × 2 mm in a growth period of over 30 days. The morphology of grown crystal has shown its growth. GSN crystals have tetragonal shape with 6 developed faces which have been shown in Fig. 1. Crystal planes and directions are generated by using WinXMorph software.

3. Results and discussion

3.1. XRD analysis

The samples were characterized by X-ray diffraction with a Bruker D8 Advance Cu Kα ($\lambda = 1.5405$ Å) at room temperature. The obtained powder XRD data was analysed using X'Pert High Score Plus and Checkcell software for calculating cell parameters and refining the obtained cell parameters, respectively. The refined values were found to be of monoclinic (space group Cc) with $a = 14.4294 \pm 0.0316$ Å, $b = 5.4095 \pm 0.0034$ Å, $c = 9.1403 \pm 0.0240$ Å, $\alpha = 90°$, $\beta = 118.900° \pm 0.174°$ and $\gamma = 90°$ and V = 626.390 Å^3 which is in good agreement with earlier reported value [11]. Fig. 2 shows the diffraction pattern and *hkl* planes for GSN single crystal.

3.2. Thermal analysis

The thermal studies of the crystals were determined by thermogravimetric analysis and differential thermal analysis. TGA/DTA analysis of GSN has been shown in Fig. 3. The TG/DTA response curves for the GSN powder sample were in the temperature range from 50 °C to 600 °C at the heating rate of 10 °C/min in nitrogen atmosphere. In the TGA curve, it was inferred that GSN is stable up to 209.72 °C as there is no appreciable weight loss till this temperature (Fig. 3). There is a sharp endothermic peak in DTA curve at 225.12 °C which has been assigned as the melting point of the crystal [12]. In the DTA curve we did not observe any peak at 56 °C which is the temperature for ferroelectric to paraelectric phase transition of glycine sodium nitrate crystal. Ideally, a heat exchange at any transition should give its indication in DTA curve. However, if the associated temperature change is very small then it may cause only a small deviation in the linearity of the curve which, due to lower sensitivity of DTA, may remain unobservable. However, *P*–*E* loop confirmed the ferroelectric to paraelectric phase transition at 56 °C as observed in the dielectric studies as well.

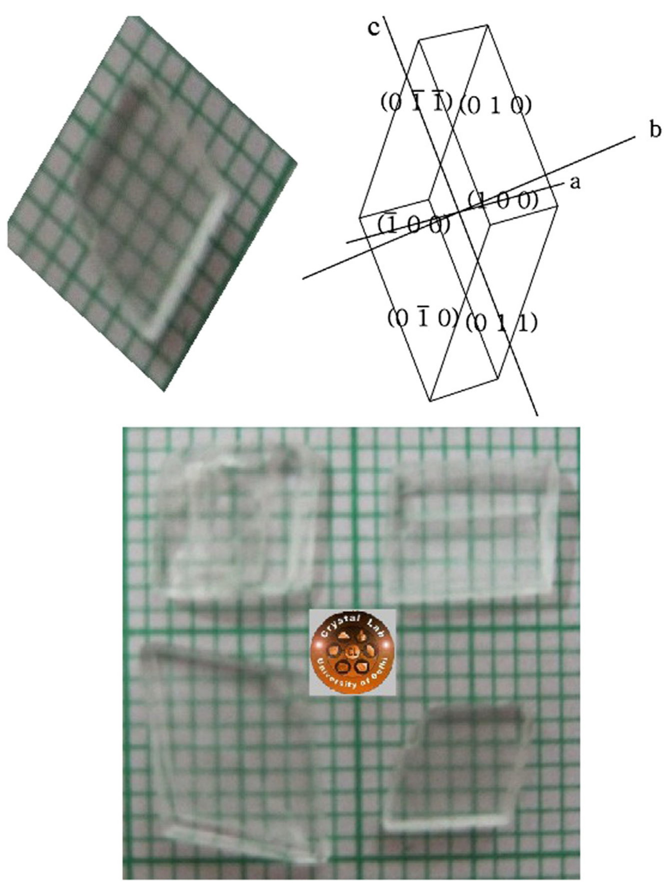

Fig. 1. The photographs and morphology of GSN crystal grown by slow evaporation method.

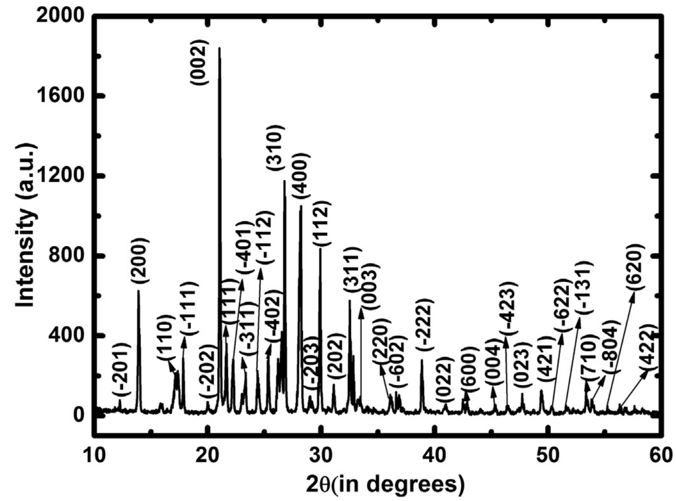

Fig. 2. The indexed pattern of powder X-ray diffraction which determined monoclinic structure of GSN.

3.3. Dielectric studies

Dielectric measurements were performed using a computer controlled E4980A LCR meter in the frequency range 20 Hz–2 MHz

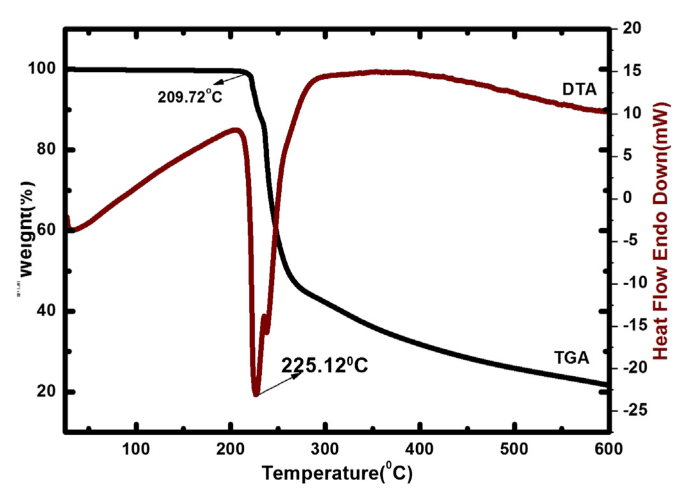

Fig. 3. DTA–TGA curves for GSN. The sharp endothermic peak in DTA curve at 225.12 °C shows the melting point of the crystal.