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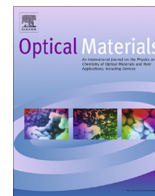
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Reversible phase transition in semi-organic compound p-Nitroanilinium sulfate detected using second harmonic generation as a tool



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ARTICLE INFO

Article history:

Received 30 June 2015

Accepted 27 July 2015

Keywords:

Nonlinear optics

Phase transition

SHG

DSC

Hybrid compounds

Hydrogen bonds

ABSTRACT

Crystals structure of p-Nitroanilinium sulfate, ($C_6H_7N_2O_2^+$, HSO_4^-) grown from aqueous solution were characterized by single crystal X-ray diffraction at 298 K. This compound crystallizes in $P2_12_12_1$ space group of orthorhombic system. The structure is built by chains formed by ($NH_3C_6H_4NO_2^+$) organic cations between which are situated the sulfate mineral anions (HSO_4^-). The thermal analyses were realized by differential scanning calorimetry (DSC) technique which indicated that the p-Nitroanilinium sulfate present a reversible phase transition at $T_c = 338(2)$ K. The SHG measurements were realized at room temperature as well as with temperature depending. During heating and cooling processes the second harmonic signals show a reversible phase transition at 57 °C. These results are in good agreement with the results obtained from DSC measurements.

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1. Introduction

In the last twenty years many investigations were established on the nonlinear optical (NLO) properties of organic molecules with great potential for optoelectronic and photonic applications [1,2]. The molecular crystals with a non-centrosymmetric arrangement are favorable for second harmonic NLO properties.

Considerable number of polar organic molecules have been studied for their potential applications in quadratic nonlinear optics including electro-optic modulation, second harmonic generation (SHG), optical switching and optical limiting [3,4]. For a long time molecular structure of p-Nitroaniline has been the subject of various investigations [5–9] because it presents one of the simplest polar molecule push–pull D- π -A system having electron donor and acceptor moieties connected by an aromatic ring which present a large NLO properties [10,11]. However, their use for applications is limited by their rather poor thermal and mechanical stabilities as well as the lack of sufficiently large single crystals of good optical quality.

Among hybrid NLO materials, the semi-organic compounds are one of the important category. The combination of organic compounds with mineral acids gives birth the new semi-organic crystals with great potential applications in NLO devices. Semi-organics materials are mainly judged by their promising properties and also by their easy growth in crystal form from aqueous solution afterward their structures can be characterized on single crystal by X-ray diffraction [12–19]. Hybrid semi-organic materials with phase transition were intensively studied for their potential applications in the data storage, signal processing, sensing, rewritable optical data storage, etc. [20–22]. Recently, in the hybrid materials were observed the reversible disorder transformation of their structure using second harmonic generation technique with excellent response of quadratic nonlinearity [23,24].

In this paper, we present the results of the X-ray single-crystal diffraction and the second harmonic generation of the p-Nitroanilinium sulfate [$C_6H_7N_2O_2^+$, HSO_4^-] compound. This material crystallizes in a non-centrosymmetric $P2_12_12_1$ group and grows from aqueous solution. The results obtained from the thermal differential scanning calorimetry (DSC) of the studied compound are also reported. A reversible phase transition at $T_c = 338(2)$ K was observed and confirmed by temperature-dependence measurements using DSC and SHG techniques.

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2. Experiments

2.1. Preparation

Single crystals of a new semi-organic compound salt: p-Nitroanilinium sulfate crystals were prepared by slow evaporation at room temperature of diluted aqueous solutions containing p-Nitroaniline (99%, Aldrich) with sulfuric acids (in a molar ratio of 1:1).

2.2. X-ray

Single-crystal diffraction experiment was carried out using the high-resolution home diffractometer equipped with an area detector. Data sets were collected at room temperature (293 K) Mo K α radiation ($\lambda = 0.71073$ Å). The compound crystallizes in a space group $P2_12_12_1$ of orthorhombic system with cell parameters respectively: $a = 6.7037(3)$ Å, $b = 9.1978(2)$ Å, $c = 14.8209(3)$ Å, $V = 913.85(5)$ Å³. The crystal structure was solved by direct methods using SIR92 (WINGX) [25] and refined by a full matrix least-square method using SHELXL97 [26]. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located by Fourier difference map and refined with isotropic thermal parameters. Details of the collected parameters, crystallographic data and final agreement factors are presented in Table 1. All hydrogen bonds are listed in Table 2.

2.3. SHG measurements

Electronic contribution to second order nonlinear optical susceptibility of the studied compounds was evaluated by second harmonic generation (SHG) method. The experiment was performed based on the work of Kurtz and Perry [27] using powder form of

Table 2

Hydrogen bonds for p-Nitroanilinium sulfate [Å and deg].

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
O1–H(1)...O(3)	0.98 (5)	1.72 (6)	2.582 (5)	146
N1–H(11)...O(4)	0.89	1.94	2.786 (5)	158
N1–H(12)...O(2)	0.89	2.00	2.840 (5)	158
N1–H(13)...O(2)	0.89	2.06	2.851 (4)	148
C3–H(3)...O(1)	0.93	2.41	3.293 (5)	158
C6–H(6)...O(6)	0.93	2.46	3.288 (5)	148

studied materials. Q-switched Nd:YAG laser working at 1064 nm with 16 ps pulse duration, 10 Hz repetition rate and 1.6 mJ power per pulse was used in this method as a source. The samples were mounted on a rotating stage with the beam focalized to ensure nonlinear effects. The second harmonic (SH) generated signal was firstly weakened by density filters and then selected using an interference filter (532 nm) before reaching the photomultiplier tube (Model: Hamamatsu). A portion of the input beam was picked off and measured by a fast photodiode to monitor the input energy. The angular dependence of the SH intensity leads to the so-called Maker fringes [1,2]. The experiment was calibrated using POM (3-methyl-4-nitropyridine-1-oxide) in powder form which is frequently used like reference material for SHG measurements.

3. Results and discussion

3.1. Structures and crystal packing

The asymmetric unit of p-Nitroanilinium sulfate compound consists of one cation p-Nitroanilinium ($C_6H_7N_2O_2^+$) and one anion (HSO_4^-) sulfate which is presented in Fig. 1.

The projection of the structure on the plan (a , c) (see Fig. 2) shows that this one is formed by chains along the direction a . These chains are constituted by the organic cations ($NH_3C_6H_4NO_2^+$) between which are situated the sulfate mineral anions (HSO_4^-). These ions are connected between them by strong hydrogen bonds.

The cohesion and the stability of the structure are insured by a three-dimensional network of two different kinds of hydrogen bonding interactions N–H...O and O–H...O.

The environment of the atom of sulfur is a tetrahedron and forms the covalent bonds with the atoms of oxygen. The sulfate HSO_4^- tetrahedron is characterized by two types of S–O bonds. Three short and one long

- One long S–O(D) bond [$S1-O1 = 1.54(3)$ Å] corresponds to the atom of oxygen donor.
- Three short S–O(A) bonds [$S1-O2 = 1.446(3)$ Å, $S1-O3 = 1.445(3)$ Å, $S1-O4 = 1.414(3)$ Å] correspond to the atoms of oxygen acceptor.

Two types of angles of O–S–O bonds are observed in the sulfate grouping HSO_4^- . The maximal values can be observed for the atoms of acceptors. The average values of angles are between atoms of oxygen acceptors and oxygen donors.

The anionic part HSO_4^- develops in chain along a and b directions (see Fig. 3).

The aryl grouping possesses a plane geometry disubstituted in C1 and C4 positions. Nitro ($-NO_2$) group on the position of C4 atom is coplanar to the aryl group and an ammonium group on the position of C1 atom. The cations groupings develop in the chains of layers parallel to the [100] direction. The projection on the plan (a , c) show the cationic layer (see Fig. 4).

The lengths of C–C bonds of the aryl group is comparable to the results found in the literature with an average distance of C–C

Table 1
Crystal data and structure refinement for p-Nitroanilinium sulfate.

$C_6H_8N_2O_6S$	$Z = 4$
$M_r = 236.20$	$F(000) = 460$
Orthorhombic, $P2_12_12_1$	$D_x = 1.717$ Mg m ^{−3}
Hall symbol: P 2ac 2ab	Mo K α radiation, $\lambda = 0.71073$ Å
$a = 6.7037(3)$ Å	$\mu = 0.36$ mm ^{−1}
$b = 9.1978(2)$ Å	$T = 293$ K
$c = 14.8209(3)$ Å	Prism, colorless
$V = 913.85(5)$ Å ³	$0.15 \times 0.12 \times 0.10$ mm
Data collection	
KappaCCD diffractometer	$R_{int} = 0.061$
Graphite monochromator	$\theta_{max} = 27.5^\circ$, $\theta_{min} = 3.5^\circ$
φ scans	$h = -7 \rightarrow 8$
4820 measured reflections	$k = -11 \rightarrow 11$
2004 independent reflections	$l = -19 \rightarrow 13$
1214 reflections with $I > 2\sigma(I)$	
Refinement	
Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighboring sites
$R[F^2 > 2\sigma(F^2)] = 0.057$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.131$	$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 0.1188P]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
2004 reflections	$(\Delta/\sigma)_{max} = 0.001$
139 parameters	$\Delta\rho_{max} = 0.33$ e Å ^{−3}
0 restraints	$\Delta\rho_{min} = -0.33$ e Å ^{−3}
Primary atom site location:	Absolute structure: H.D. Flack, Acta Cryst. A39 (1983) 876–881
structure-invariant direct methods	Absolute structure parameter: 0.44 (16)

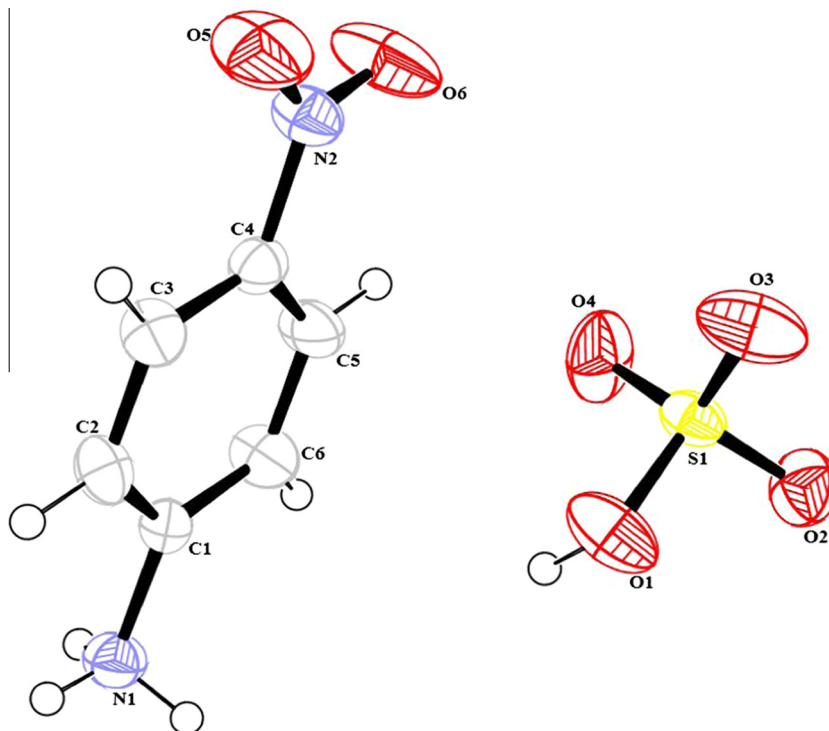


Fig. 1. Asymmetric unit of p-Nitroanilinium sulfate compound.

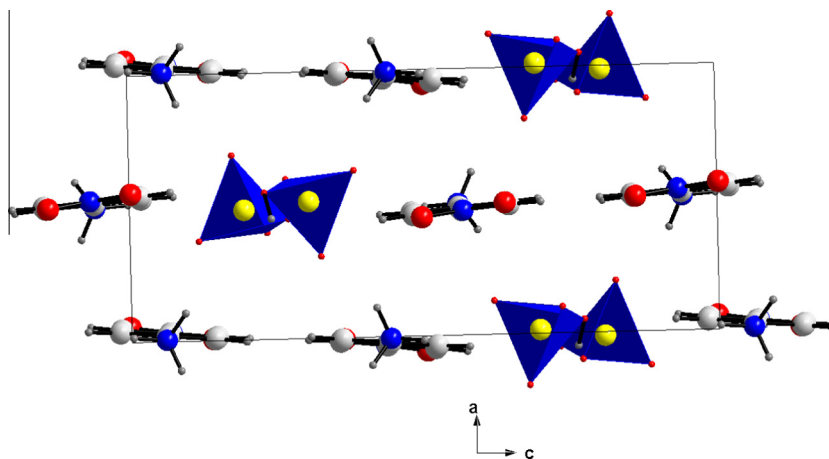


Fig. 2. Packing diagram of the structure along the *b* axis.

bonds of 1.375 Å and an average of angle of 120°. The N2 atom of nitro group has a Sp^2 hybridization, and it is connected to two covalent bonds with O5 and O6 oxygen atoms with the distance of bonds of 1.20 Å and the angle of 122.8(4)°.

The environment of the nitrogen atom of the ammonium grouping is regular tetrahedron.

The organic cations and the mineral anions are connected between them by strong interactions type N–H...O and O–H...O giving birth to a three-dimensional network of hydrogen bonding.

Three types of hydrogen bonds are observed in this compound:

1. One hydrogen bond of the category S–O–H...O–S is observed between the sulfate HSO_4^- groupings via the interaction O(1)–H(1)...O(3) [2.582 (5) Å] (see Fig. 5).
2. Four interactions anion–cation are observed, between three the hydrogen of the ammonium grouping and the oxygen atoms of sulfate grouping (N1–H11...O4 = 2.786 (5) Å, N1–H12...O3 = 2.840 (5) Å and N1–H13...O2 = 2.851 (4) Å), and enters the atom carbon C3 with the sulfate grouping (C3–H3...O1 = 3.293 (5) Å) (see Fig. 5).
3. The organic cations are connected between them by the hydrogen bond via the hydrogen atom of C6 and the atom O6 of nitro grouping [C6–H6...O6 = 3.288 (5) Å].

All hydrogen bond parameters are summarized in Table 2.

3.2. NLO properties

The combination of organic compounds with mineral acids gives birth to new semi-organic crystals presenting strong NLO properties. The crystals of the p-Nitroanilinium sulfate compound $[(C_6H_7N_2O_2)^+, HSO_4^-]$ are obtained by slow evaporation of an aqueous solution 1:1 of p-Nitroaniline ($C_6H_6N_2O_2$) and sulfuric acid (H_2SO_4).

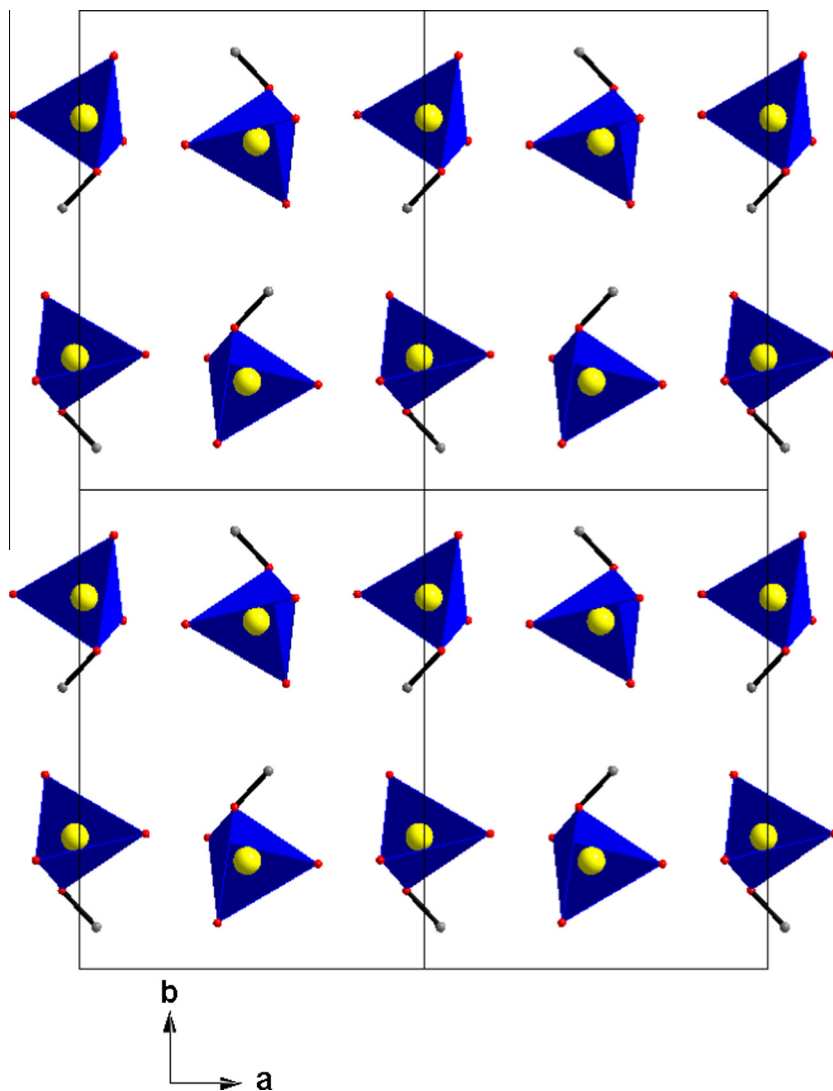


Fig. 3. Packing diagram of the sulfate anions along the *c* axis.

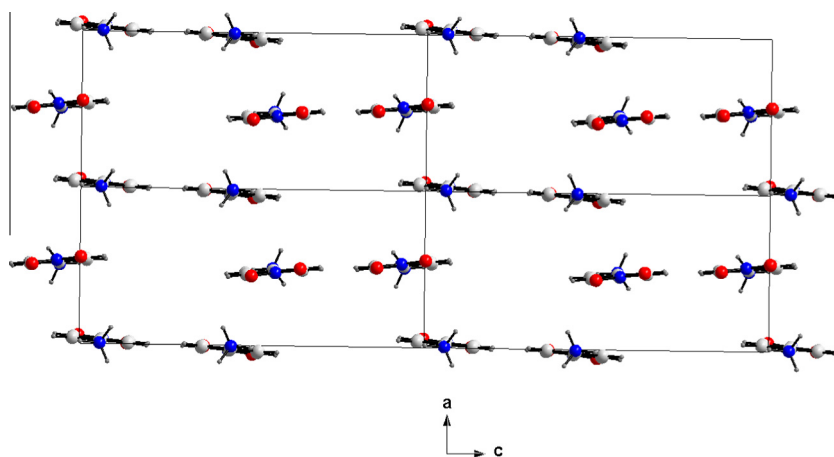


Fig. 4. Packing diagram of the p-Nitroanilinium cations along the *b* axis.

The compound crystallizes in non-centrosymmetric space group $P2_12_12_1$ of orthorhombic system. The values of the effective second order nonlinear susceptibility were determined by measuring second harmonic intensities as a function of incident angle

between -50° and 50° on the polycrystalline powder of compound (I) using the Kurtz and Perry model. The synthesized product were crushed in a mortar and pressed between two glass blades for SHG measurements. The experiment was calibrated and verified by

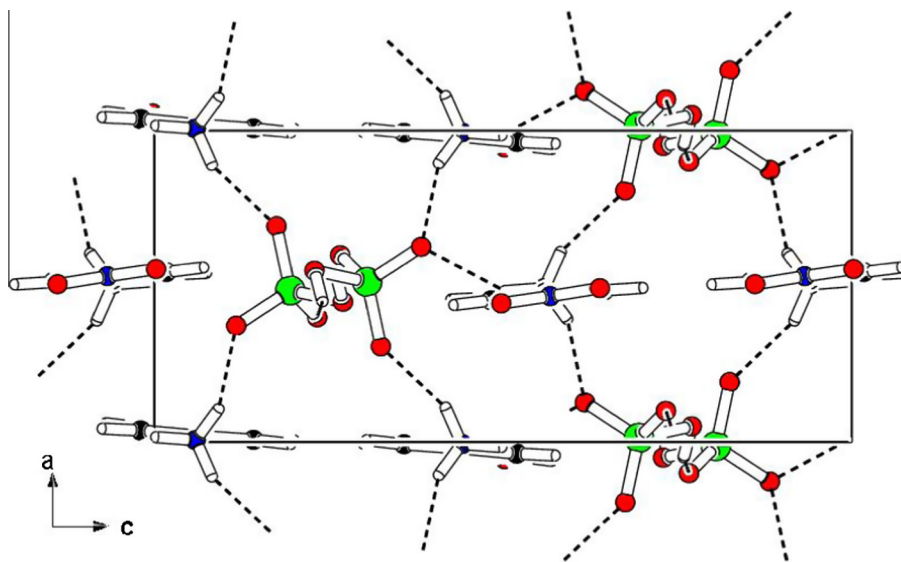


Fig. 5. The molecular packing of the structure viewed along the *b* axis, showing the hydrogen bonding interactions.

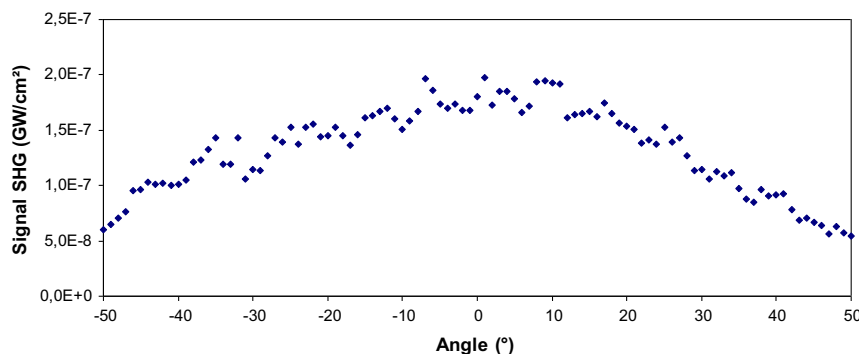


Fig. 6. Second harmonic intensity as a function of the incident angle for studied compound.

using POM ($\chi_{\text{eff}}^{(2)} = 12 \text{ pm/V}$, at $\lambda_{\omega} = 1064 \text{ nm}$ [28–30]) which is frequently used like reference material for SHG measurements.

We observed that the maximum of intensity is for all the materials studied in the position 0° (see Fig. 6). This is the position of the sample placed perpendicularly to the fundamental beam.

For a constant input intensity and no dispersion, the effective nonlinear susceptibility, $\chi_{\text{eff}}^{(2)}$, of the samples is related with that of the reference plate $\chi_{\text{eff}}^{(2)}$ using the following equation [31,32]:

$$I_{2\omega} = \frac{2\pi^2}{n_1^2 n_2^2 \lambda_1^2 c \epsilon_0} |\chi^{(2)}|^2 I_{\omega}^2 L^2 \frac{\sin^2(\Delta k L/2)}{(\Delta k L/2)^2}$$

where $\chi^{(2)}$ is the second order nonlinear susceptibility, n_1 , n_2 are refractive indices for frequency ω and 2ω , respectively, L is the thickness of the sample and Δk is the phase mismatch between waves at ω and 2ω .

The value of the second order nonlinear susceptibility $\chi_{\text{eff}}^{(2)}$ for the p-Nitroanilinium sulfate was estimated to 1.15 pm/V and this value is about 10% of that of the POM.

4. DSC analyses of PNA

The DSC analyses were obtained using a Perkin Elmer model 8500 differential scanning calorimeter. The measurements were performed between 0 and 90°C . The curves of DSC are represented

in Fig. 7. It shows one reversible structural (heating/cooling) characterized by an exothermic and endothermic peak at 54.74 and 55.67 respectively corresponding to a reversible phase transition of non-centrosymmetric/centrosymmetric space group and also confirms the results obtained by SHG measurements as a function of temperature.

The measures of the SH signal according to the temperature were realized on the range 20 – 80°C with a speed heating and cooling of 3°C/min . The curves SH according to the temperature were represented in Fig. 8. It shows that during the heating process the SH signal decreases from 50 to 60°C up to the disappearance of the SH signal at 65°C . This gives some explanation by the passage of a non-centrosymmetric space group to a centrosymmetric space group, which confirms that this compound present a phase transition at 57°C . For the cooling process to the SH signal we observe that the curve in good agreement with the heating curve but in the opposite sense. This result confirms that the phase transition is reversible.

5. Conclusion

In this work, we presented the results on the thermal and second harmonic generation measurements at room temperature and dependence-temperature of one non-centrosymmetric new semi-organic compound. The crystals of studied compound were obtained from solution aqueous at room temperature and

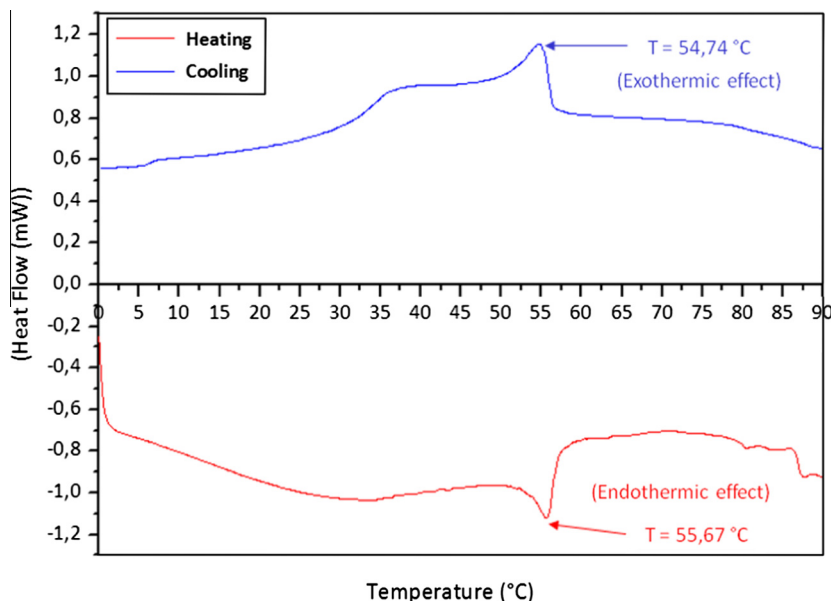


Fig. 7. Calorimetric measurements.

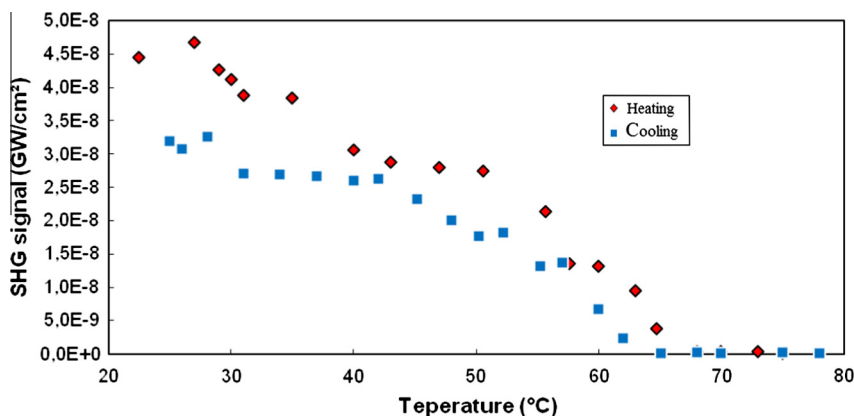


Fig. 8. Second harmonic generated signal (SH) of powder polycrystalline of studies compound driven by temperature.

characterized by single crystal X-ray diffraction at 298 K. This compound crystallizes in $P2_12_12_1$ space group of orthorhombic system. The structure is formed by chains formed by $[\text{NH}_3\text{C}_6\text{H}_4\text{NO}_2^+]$ organic cations between which are situated the sulfate mineral anions $[\text{HSO}_4^-]$. The cohesion and the stability of the structure are insured by a three-dimensional network of two different kinds of hydrogen bonding interactions $\text{N-H}\cdots\text{O}$ and $\text{O-H}\cdots\text{O}$.

The DSC measurements were performed between 0 and 90 °C. Reversible structural (heating/cooling) characterized by an exothermic and endothermic peak at 54.74 and 55.67 respectively corresponds to a reversible phase transition.

The values of the effective second order nonlinear susceptibility $\chi_{\text{eff}}^{(2)}$ were determined by measuring second harmonic intensities as a function of incident angle on the polycrystalline powder of compound using the Kurtz and Perry model. The value of $\chi_{\text{eff}}^{(2)}$ for the p-Nitroanilinium sulfate was estimated to 1.15 pm/V. The measures of the SH signal according to the temperature were realized on the range 20–80 °C with a speed heating and cooling of 3 °C/min. During the heating and the cooling process the SH signal disappear and reappear at 65 °C. This gives some explanation by the passage of a non-centrosymmetric space group to a centrosymmetric space group, which confirms that this compound present a reversible phase transition at 57 °C.

Appendix A. Supplementary material

CCDC 670079 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.optmat.2015.07.035>.

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