

Full Length Research Paper

Physico-chemical properties of Alanine-Sodium nitrate: An optical overview

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Accepted 16 May, 2011

Single crystals of the semi organic materials L-Alanine sodium nitrate (LASN) and D-Alanine sodium nitrate (DASN) were grown from an aqueous solution by slow evaporation technique. X-ray diffraction (XRD), studies were carried for the doped grown crystals. The absorption of these grown crystals was analyzed using UV-vis-NIR studies, and it was found that these crystals possess minimum absorption from 200 to 1100 nm. An infrared (FTIR) spectrum of single crystal has been measured in the 4000-400 cm^{-1} range. The assignment of the observed vibrational modes to corresponding symmetry type has been performed. A thermo gravimetric study was carried out to determine the thermal properties of the grown crystal. The efficiency of second harmonic generation was obtained by a variant of the Kurtz-Perry method.

Key words: Nonlinear optical, second harmonic generation, Alanine sodium nitrate.

INTRODUCTION

Nonlinear optics has emerged as one of the most attractive fields of current research in view of its vital applications in areas such as optical modulation, optical switching, optical logic, frequency shifting, and optical data storage for the developing technologies in telecommunication and signal processing (Anandha and Ramasamy, 2009). Extensive studies have been made on the synthesis and crystal growth of nonlinear optical (NLO) materials (Uma et al., 2008).

Semiorganic materials possess several attractive properties such as high NLO coefficient, high laser damage threshold and wide transparency range, high mechanical strength and thermal stability, which make the materials suitable for second harmonic generation (SHG) and other NLO applications (Shethuraman et al., 2008).

Organic materials have been of particular interest because the NLO responses in this broad class of materials in microscopic origin, offers an opportunity to use theoretical modeling coupled with synthetic flexibility to design and produce novel materials (Uma et al., 2008).

Amino acids are the potential candidates for optical

second harmonic generation (SHG) because they contain chiral carbon atom and crystallize in noncentro symmetric space groups (Praveen et al., 2008). A series of studies on semiorganic aminoacid compounds such as L-arginine phosphate (LAP), L-arginine hydrobromide (L-AHBr), L-histidine tetrafluoroborate (L-HFB) (Shethuraman et al., 2008) L-arginine hydrochloride (L-AHCl), (Meera et al., 2004) L-alanine acetate (L-AA) (Mohan et al., 2005) and glycine sodium nitrate (GSN) (Narayan and Dharmaprasanth, 2002) as potential NLO crystals have been reported. Alanine is an amino acid which forms a number of compounds on reaction with inorganic acid and salts to produce an outstanding material for NLO applications (Shethuraman et al., 2008). The compound was first crystallized by Bernal and later by Simpson et al. It belongs to the orthorhombic crystal system (space group P212121) with a molecular weight of 89.09 and has a melting point of 297°C (Vijayan et al., 2006).

The compounds, L-alanine sodium nitrate and D-alanine sodium nitrate were obtained as the product by reaction of sodium nitrate and the amino acids L-alanine and D-alanine in aqueous solution. In the present investigation, single crystals were grown and characterized by X-ray diffraction powder, Fourier transform infrared (FTIR) spectroscopic studies, Thermo gravimetric analysis (TGA/DTA), UV-Vis-NIR spectral analysis and

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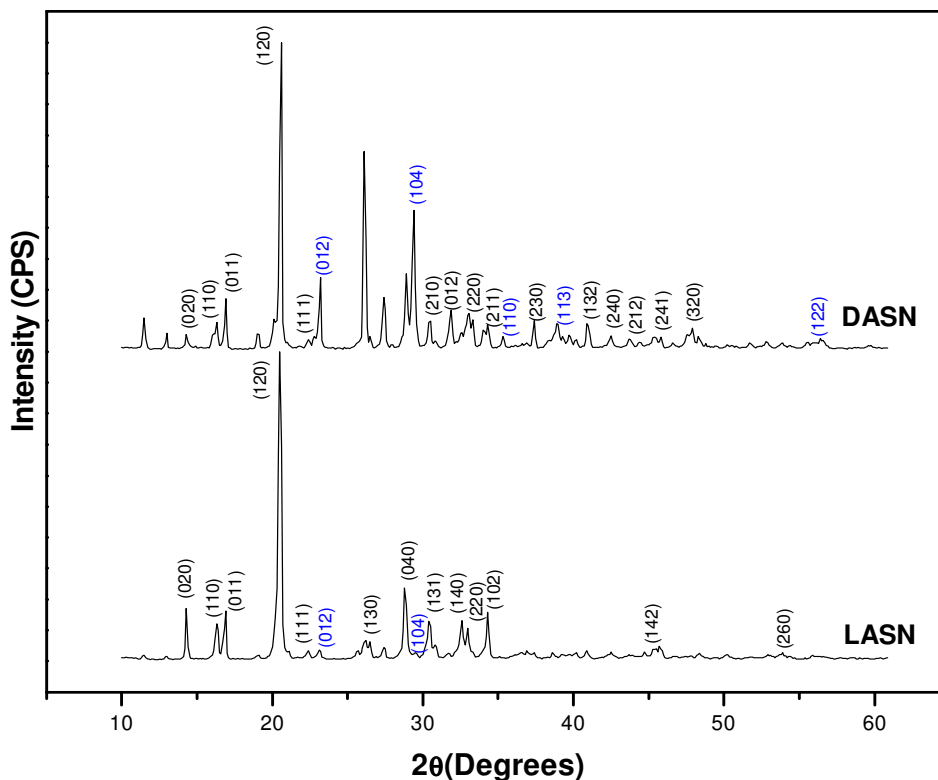


Figure 1. Powder X-ray diffractogram of L-alanine sodium nitrate (LASN) and D-alanine sodium nitrate (DASN).

the efficiency of second harmonic generation (SHG).

EXPERIMENTAL DESIGN

The crystals obtained during the development of this work were grown by slow evaporation technique at room temperature through an aqueous solution. The reactive commercially available L-alanine and D-alanine $C_3H_7NO_2$ were used with stoichiometry Sigma-Aldrich Lab with 98% purity and molecular weight 89.09 g/mol and the sodium nitrate $NaNO_3$ stoichiometry Sigma-Aldrich Lab with 99.9% purity and molecular weight 84.99 g/mol. The samples were prepared using 1:1 molar ratio in distilled water and constant agitation for 35 min and a temperature of 60 °C. The evaporation time for the L-alanine sodium nitrate solution at room temperature was 45 days and 60 days for the D-alanine solution.

The Phillips Expert powder X-ray diffractometer with Cu K α radiation ($\lambda = 1.5428 \text{ \AA}$) was used for the powder X-ray diffraction pattern. The sample was scanned in the 2θ values ranging from 10 to 60 at the rate of 0.05°/min.

In order to analyze the presence of functional groups, FTIR spectrum was recorded in the range of 400 cm^{-1} to 4000 cm^{-1} using a MAGNO IR 750 series II NICOLET spectrometer. The samples were added to a matrix of KBr to perform this procedure.

The UV-vis spectra gave limited information about the structure of the molecule because the absorption of UV and visible light involves promotions of the electrons in the σ and π orbitals from the ground state to higher energy states. The transition spectrum is very important for any NLO material because it can be of practical use only if it has a wide transparency window. NLO materials have a practical use only if they have a wide transparency state. To find

this absorbance window, a Lambda 10 Perkin Elmer UV-Vis spectrometer was used. The scanning was done in the range of 200 to 1100 nm the same way as with the FTIR.

TGA/DTA was done in a TA Instruments STD 2960 Simultaneous DTA-TGA. The samples were heated from room temperature to more than 1000 °C at rate of 10 °C/min.

In order to find the SHG, the crystals were grown according to the Kurtz and Perry technique (Lydia et al., 2009) into powder (about 70 μm) and densely packed between two transparent microscope glass slides (Kurtz and Perry, 1968; Silverstein and Webster, 1998). Once the samples were placed into the glass slides, a Nd:YAG Quanta ray INDI series laser of 1064 nm generating an 8 ns pulse and operated at 6 mJ/pulse and at rate of 10 Hz is pumped at the proper angle and distance in order to see SHG on green color (532 nm) that corresponds to the expected emitted light and it is the half wavelength of the incoming light.

RESULTS AND DISCUSSION

X-ray diffraction

The resultant peaks in the diffractogram (Figure 1) show an intense peak at 20.54°, which coincides with the plane (120) and the reflections of the planes (020), (110), (040), (140), (111), (220), (102), (131), (142) and (260), corresponding to the principal planes of the L-alanine present in the L-alanine sodium nitrate, where the planes (012) and (104) were identified with nitrate. The peaks appearing in the spectrum that have not been

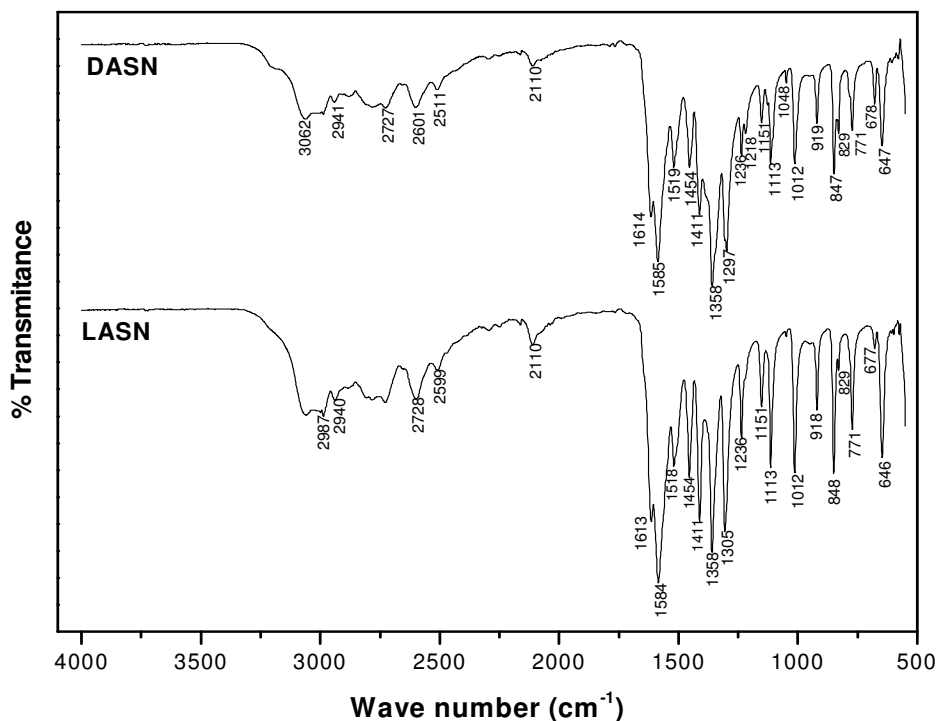


Figure 2. FTIR spectrum of LASN and DASN.

identified can be attributed to the formation of the L-alanine sodium nitrate compound. In both the L-alanine and D-alanine cases, the presence of an intense peak at 20.59° which coincides with the plane (120) and reflections from planes (020), (110), (011), (111), (210) (012), (220), (211), (230), and (241), corresponding to the principal planes of the D-alanine present in the D-alanine sodium nitrate was identified. The planes (012) (104) (110) (113) and (122) were identified with nitrate. The peaks appearing in the spectrum that have not been identified can be attributed to the formation of the compound D-alanine sodium nitrate.

FT-IR study

In order to obtain the presence of functional groups, FTIR spectrum was recorded in the range of 400 cm^{-1} to 4000 cm^{-1} by using a MAGNO IR 750 series II NICOLET spectrometer.

The sample of L-alanine sodium nitrate (LASN) and D-alanine sodium nitrate (DASN) were added to a matrix of KBr to perform this procedure as shown in Figure 2. The presence of the carboxyl acid group around 3000 cm^{-1} can be observed due to the Alanine presence. The main internal vibrations of Alanine are observed on the functional groups (NH_3^+ , CH_2 , COO^-) which is in agreement with the data reported before (Lydia et al., 2009); symmetric and asymmetric bending vibrations were observed on the CH_3 groups for LASN and DASN at 2987 and 1454 cm^{-1} . The peak at 2599 and 2601 cm^{-1} is

symmetrical stretching of CH to LASN and DASN respectively. The 1151 , 1218 and 1236 cm^{-1} frequencies are attributed to the rocking deformation of the NH_3^+ group (Meera et al., 2004). Furthermore the peak 1048 cm^{-1} is a symmetrical stretching of CCN group.

Other low frequency bands are typical for N-H...O Hydrogen bonds arising from the overtones around the 2727 cm^{-1} . The rest of the functional groups: COO^- , CN and NO_3 between 500 and 1500 cm^{-1} also agree with the reported data.

Usually the presence of nitrates in the lattice can be identified by their characteristic signature in the ranges: 1660 - 1625 , 1300 - 1255 , 870 - 833 and 763 - 690 cm^{-1} (Baran et al., 2003). Parent compound traces were identified in the synthesized compound. The presence of the NO_3 group in the LASN and DASN can be identified by the peaks at 1358 , 1113 , 849 and 771 cm^{-1} . The symmetric and asymmetric NH_3^+ stretching vibrations appear at frequencies 2941 and 2110 cm^{-1} respectively. The absorption peaks at 1613 , 1584 , and 1518 cm^{-1} for LASN, and 1614 , 1585 and 1519 cm^{-1} for DASN confirm the presence of NH_3 bending. The presence of nitro groups in the spectrum confirms the LASN and DASN compounds. Other important functional groups are detailed in Table 1.

Raman spectroscopy

The Raman spectra were carried out at room temperature in frequency range 400 - 4000 cm^{-1} with Xplora

Table 1. FT-IR and Raman functional group assignments of the grown LASN and DASN.

Raman (cm ⁻¹)		FT-IR (cm ⁻¹)		Assignments
LASN	DASN	LASN	DASN	
3706				Overtone
3426				Overtone
			3062	Symmetric CH ₃ stretching
3000	3003			Asymmetric CH ₃ stretching
		2987		Symmetric CH ₃ stretching
2964	2964			CH ₂ stretching and asymmetric CH ₃ stretching
2948				Symmetric CH ₂ stretching
		2941	2941	Symmetric NH ₃ stretching
2936	2933			Asymmetric CH ₂ stretching
2888	2888			CH ₂ stretching
	2734			Overtone
		2728	2727	N-H...O and O-H...O stretching
	2603		2601	Symmetric CH stretching
		2599		Symmetric CH stretching
2512			2511	Overtone
2484				Overtone
2444	2442			Overtone
		2251		CH ₃ stretching
2123	2119			Overtone
		2110	2110	Asymmetric NH ₃ stretching
1939				Asymmetric NH ₃ deformation
1775				Asymmetric COO stretching
1659				Asymmetric NH ₃ deformation
1630				Asymmetric NH ₃ deformation
		1613	1614	NH ₃ bending
1599	1596			Asymmetric NH ₃ deformation
		1584	1585	NH ₃ bending
1571				Asymmetric COO ⁻ stretching
	1543			Overtone
1531				Symmetric NH ₃ deformation
		1518	1519	NH ₃ bending
1503				CH ₃ deformation
	1496			Overtone
1486	1489			Asymmetric COO ⁻ deformation
1466	1465			C _β H ₂ scissors mode
		1454	1454	Asymmetric CH ₃ bending
1422				CH ₃ bending
	1412	1411	1411	Symmetric C-COO ⁻ stretching
1386				CH ₃ puckering
1363	1366			Wagging CH ₂ deformation
		1358	1358	NO ₃ stretching
	1312			CH ₂ wagging
1306		1306		C-H and N-H bending
			1297	Flexed position CH ₂
	1235	1236	1236	NH ₃ ⁺ Rocking
		1218	1218	NH ₃ ⁺ Rocking
1151	1150	1151	1151	NH ₃ ⁺ Rocking and symmetric COO ⁻ stretching
1113	1112	1113	1113	NO ₃ stretching
1070				Overtone
1050		1048	1048	Symmetric CCN stretching

Table 1. Contd.

1022	1027			CH ₃ rocking
		1012	1012	Overtone of torsional oscillation NH ₃ ⁺
926				NH ₃ rocking
	936			CH ₂ rocking
		918	919	Overtone of torsional oscillation NH ₃ ⁺
853	850			N-C stretching
		849	847	NO ₃ stretching
		829	829	C-C stretching
774	774			OH deformation
		771	771	NO ₃ stretching
725				COO wagging
		677	678	NO ₃ ⁻ in plane deformation
	651	646	647	COO ⁻ in plane deformation
		578	578	Overtone

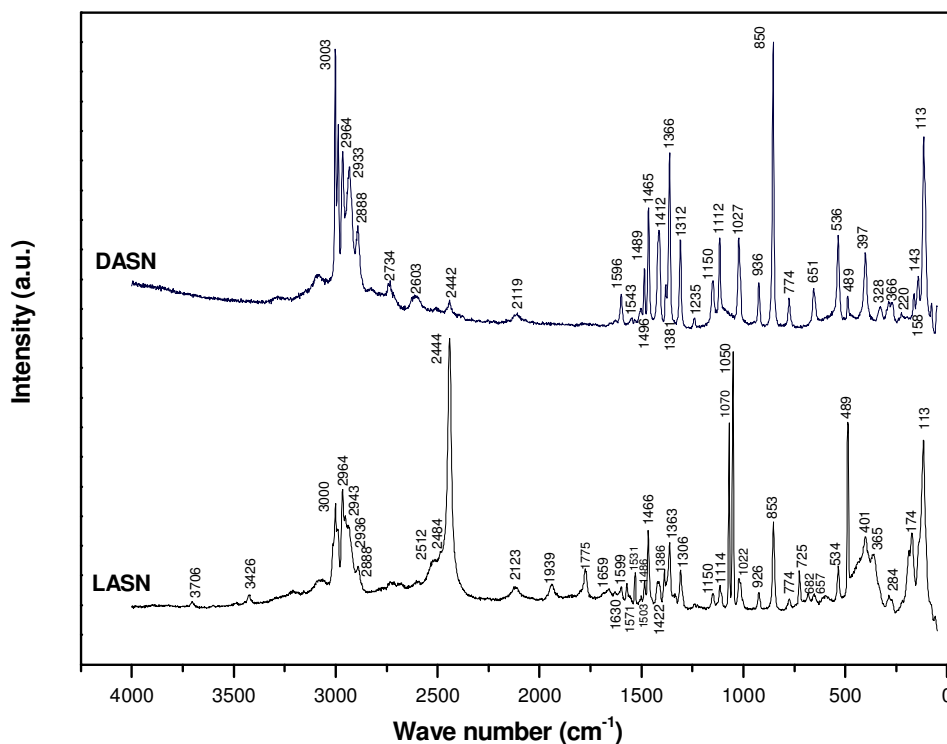


Figure 3. Raman spectrum of LASN and DASN.

Raman microscope HORIBA system. The laser Raman spectrum, showing the presence of more intense peak around 850 cm⁻¹, is due to COO⁻ stretching mode of vibrations (Figure 3). The peaks at 1113 and 1112 cm⁻¹ are assigned to NO₃ stretching.

The C-H and N-H bending vibrations are observed at 1306 cm⁻¹ as a sharp peak. The asymmetric CH₃ bending at 1422 cm⁻¹ and O-H bending is around 950 cm⁻¹ (Britto et al., 2008). The peak at 1411 cm⁻¹ is assigned to the

symmetric stretching C-COO carboxyl group.

In Raman spectra of alanine, the symmetric and asymmetric deformation vibrations of the NH₃⁺ groups appear in the region between 1680–1470 cm⁻¹ (Baran and Ratajczak, 2006); in the spectrum L-alanine and D-alanine we found in 1531 y, 1939, 1659, 1630, 1599, 1596 cm⁻¹ frequency. The position of NH₃⁺ asymmetric stretching frequency, indicate the formation of intra and inter-molecular strong N-H---O hydrogen bonding of the

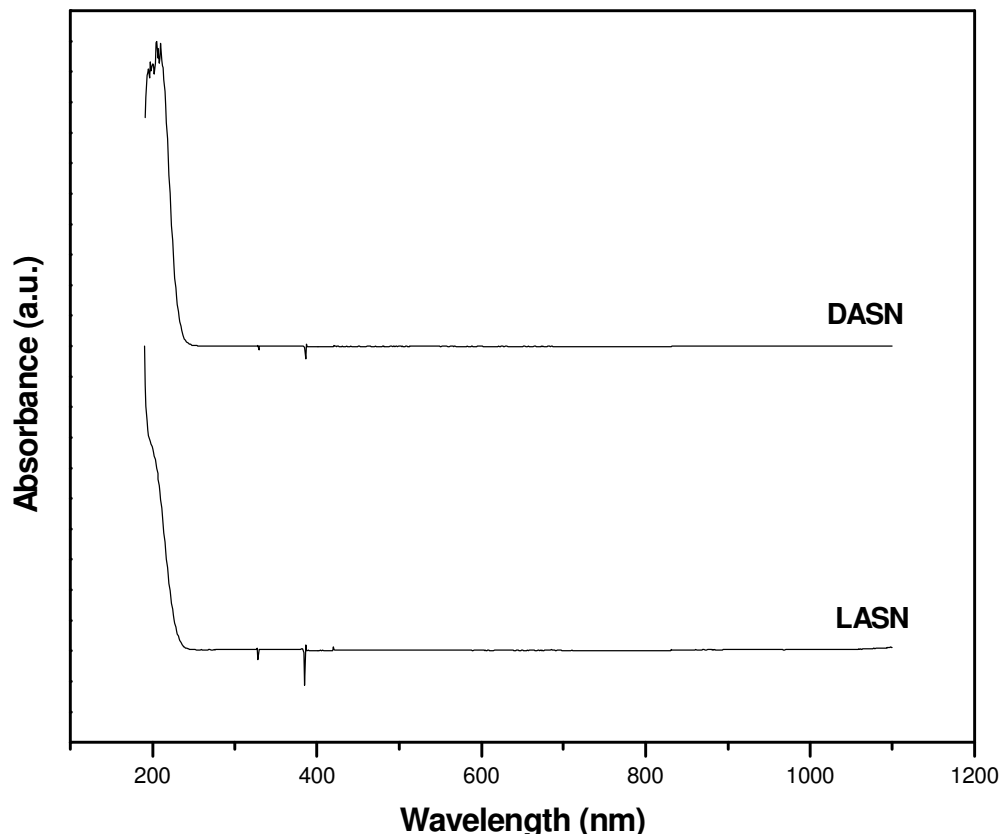


Figure 4. UV-vis spectra of the LASN and DASN.

NH_3^+ group, with the oxygen of both the carbonyl group and inorganic nitrates (Hernández-Paredes, 2008; Vijayakumar et al., 2008). The study of symmetry stretching and stretching vibration of CH_2 group is observed in 2948 and 2964, 2888 cm^{-1} . The band around 1235, 1150, 1151 and 926 cm^{-1} is also indicative of the NH_3 rocking modes. The peak at 1366 cm^{-1} is a deformation of CH_2 group, and at 1312 cm^{-1} is attributed to the CH_2 wagging. The intensity varies upon the source used for analyzing the sample. Other important functional groups are detailed in Table 1.

UV-vis study

Figure 4 shows the absorbance zone above 250 nm (Ultra-violet wavelength) where a wide band completely transparent in all the visible range is observed (Infrared wavelengths) (Lydia et al., 2009; Martin and Natarajan, 2008; Ramesh et al., 2006). This means that this material presents a good non-absorbance band in the visible range for expected applications. A little protuberance around the 300 nm is observed (Narayan and Dharmaprakash, 2002; Narayan 2002). This little peak is still outside the visible zone (UV zone) and it could

present some absorbance if the crystal were to be excited with 600 nm (red color) trying to obtain a second harmonic of 300 nm (UV color). Other noticeable characteristic in the absorption spectrum is a wide transparency window within the range of 400–1100 nm which is desirable for NLO crystals because the absorptions in an NLO material near the fundamental or second harmonic signals will lead to the loss of the conversion of SHG. Due to this property, LASN and DASN have potential uses for SHG using an Nd: YAG laser (1064 nm) to emit a second harmonic signal within the green region (532 nm) of the electromagnetic spectra.

Thermal analysis

Figure 5 shows the TGA pattern of the LASN and DASN showing good stability below 220°C with a rapid dropping beyond that temperature (Lydia et al., 2009; Ambujam et al., 2006). Figure 4 also shows the DTA pattern of LASN where an exothermic transition appears at about 230°C. Meanwhile, it is pure and presents another endothermic transition at 400°C (Lydia et al., 2009; Ambujam et al., 2006). Within this temperature range, the possible NLO applications becomes promising due to the use of laser

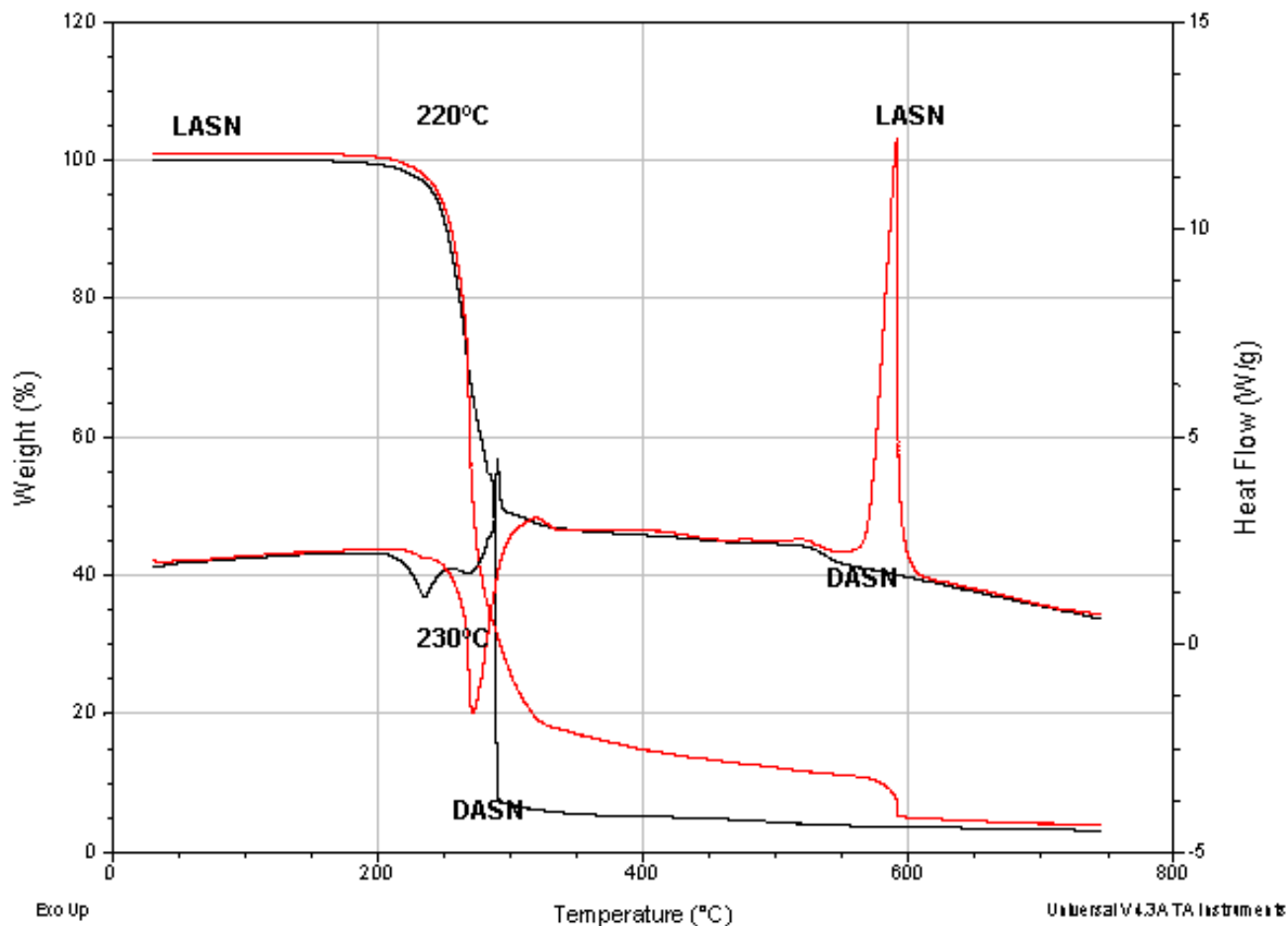


Figure 5. TGA and DSC curves of LASN and DASN.

powers, for LASN and DASN performing below 230°C.

SHG signal detection

Figure 6 shows the data collected from the detector where the SHG signal is plotted vs the beam energy. This kind of experiments has been used in order to measure the damage threshold. In this case, the SHG intensity tends to increase when the beam energy is also increased. This experiment shows the good quality of these crystals for the second harmonic generation, but there is a better efficiency in the LASN sample.

Conclusions

A new non-linear optical semiorganic crystal, LASN and DASN were synthesized. The single crystals were grown from an aqueous solution. Functional groups of good quality crystals of LASN and DASN grown by the slow

evaporation technique have been detected by FTIR and Raman spectroscopies.

Also based on UV-vis spectra observations, an absorption zone below the 250 nm (Ultra-violet wavelengths) can be seen recovering a good transmittance values across all the visible range until near IR frequencies and beyond. This situation shows these crystals can be used for applications involving the band of visible light. The transparency of the crystal in the visible and infrared regions shown in transmission spectra confirms the NLO property of this.

Other characterization was the thermal response. The TGA/DTA results show a degrading temperature about 230°C which promises to have good applications at high temperatures, revealing that the crystal is thermally stable until that temperature.

The SHG test is the first one performed in this kind of material and was observed that the SHG intensity tends to be directly proportional to the beam energy and follows a linear tendency with a positive slope which promises to be a good non-linear optical material.

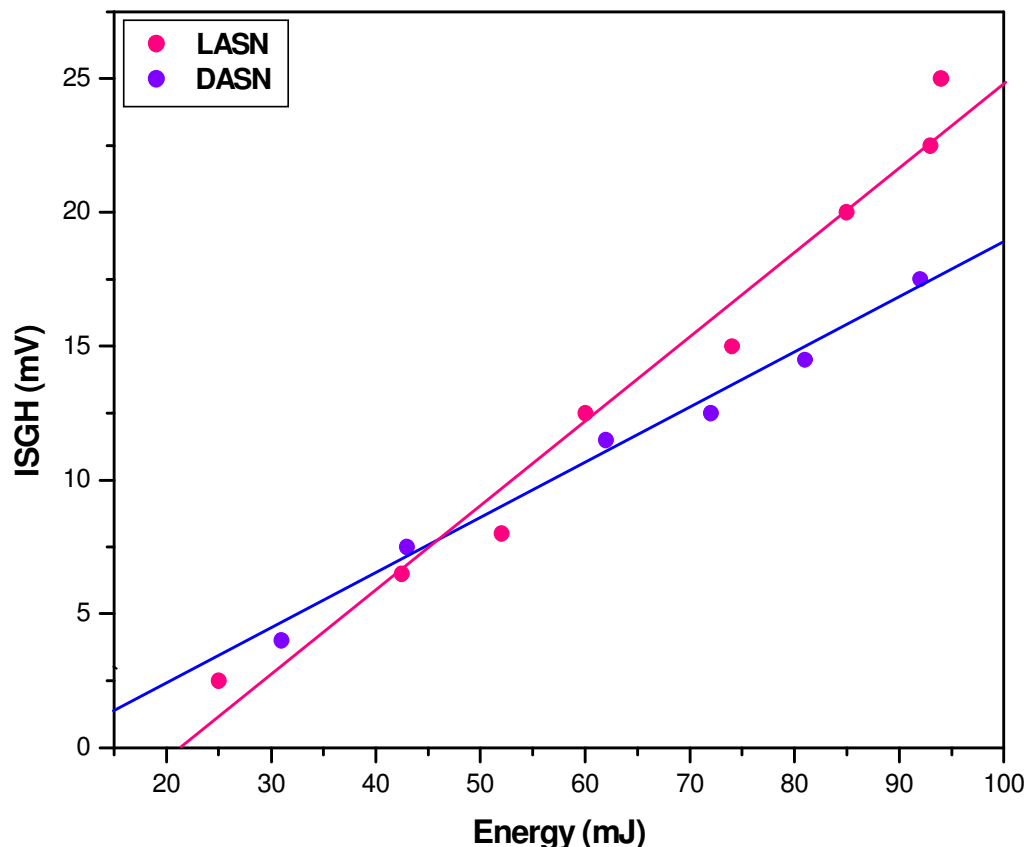


Figure 6. Linear fit for the SHG intensity as function of the beam energy.

Finally, we succeeded in obtaining good quality crystals of LASN and DASN and for the first time, the second harmonic generation was detected in this material which indicates that these crystals are new materials with non-linear optical properties with potential applications.

ACKNOWLEDGMENTS

Authors thank the National Council of Science and Technology of Mexico for its financial support. Also to National Laboratory of Nanotechnology of CIMAV, S.C., at Chihuahua, Mexico. The authors are very grateful to Enrique Torres Moye (M. Sc) (X-ray Laboratory), Daniel Lardizabal (M. Sc) (Thermal Analysis Laboratory), Luis de la Torre (Uv-vis analysis) and Antonio Silva Molina (Raman study).

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