Research Paper

INFLUENCE OF MOLECULAR AND CRYSTAL STRUCTURE ON NONLINEAR OPTICAL PROPERTIES OF HYDRATED AND ANHYDROUS POTASSIUM L-2-NITRIMINO-1,3-DIAZEPANE-4-CARBOXYLATE CRYSTALS

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Abstract

The physical properties of crystals depend on their chemical composition and their molecular and crystal structure. The presence of donor amino groups (NH_2) and acceptor nitro groups (NO_2) in a molecule can increase the molecule's non–linear optical (NLO) properties.

L-nitroarginine, in a strong alkaline environment (MOH (M=Li,Na,K), crystallizes to form L-2-nitrimino-1,3-diazepane-4-carboxylic acid (L-NIDCA·H_2O and L-NIDCA). We found that the slow evaporation of a solution of L-nitroarganine and an alkali in equimolar quantities leads to the formation of a metallic salt with L-2-nitrimino-1,3-diazepane-4-carboxylate anions (K(L-NIDC).H_2O, Na(-NIDC), L-NaNIDC, Li(L-NIDC); this salt shows strong NLO properties.

This study also addressed the second-harmonic generation of L-KNIDC·H_2O and L-KNIDC crystals and how their crystal and molecular structure affects the NLO properties.

The infrared and Raman spectra of K(L-NIDC)·H_2O and K(L-NIDC) crystals were studied with respect to these structural features. We found that the intensity of second-harmonic generation in K(L-NIDC) is 2.75 times higher than in the standard KDP crystal, while the intensity in K(L-NIDC)·H_2O is much lower.

Key words: Potassium L-2-nitrimino-1,3-diazepane-4-carboxylate, crystal structure, vibrational spectra, thermal properties, nonlinear optical activity.

1. Introduction

A main problem in materials science is understanding the interdependence between a crystal's chemical composition and molecular or crystal structure and its physical properties. To study chemical composition, initial materials can be chosen to include functional groups that will contribute to increasing of nonlinear optical (NLO) properties of a crystal. L-nitroarginine and its associated salts are known to have strong NLO properties due to the acceptor nitro groups (NO_2) and donor amino groups (NH_2) in their structure [1–5]. L-nitroarginine in a strong alkaline medium (MOH (M=K,Na,Li) cycles to produce L-2-nitrimino-1,3-diazepane-4-carboxylic acid (L-NID-CA·H_2O or L-NIDCA) [6, 7]. The metallic salt M L-nitrimino-1,3-diazepane-4-carboxylic (ML-NIDC(K(L-NIDC)·H_2O,Na(L-NIDC),Li(L-NIDC)) crystallizes from an equal-molar-ratio water solution of L-nitroarginine and alkali by slow evaporation. Both L-NIDCA·H_2O and L-NIDCA crystals and the associated salts have strong NLO properties.

Using K(L-NIDC)·H_2O, K(L-NIDC) metallic salts, we propose a new method for obtaining L-nitrimino-1,3-diazepane-4-carboxylic acid. In this method, a water solution of K(L-NIDC)·H_2O or K(L-NIDC) compounds, the potassium interacts with HBF_4 acid to produce KBF_4 salt that precipitates out

of the solution due to its low solubility (0.44 g/100 g at 20 °C).

After removing this precipitate, *L*-NIDCA·H$_2$O crystallizes from an aqueous solution by slow evaporation at room temperature. This method differs from the method reported previously [8].

L-2-nitrimino-1,3-diazepane-4-carboxylic acid was first obtained in 1961 [8] by using a method proposed in 1948 [9]. Its molecular structure was determined by chemical method [8], and in 2008 the structure of *L*-NIDCA was confirmed by X-ray structural analysis [6, 7]. The salt K(*L*-NIDC)·H$_2$O crystallizes in the *I*222 space group [10]. A crystal with such symmetry and the associated anhydrous crystal (K*L*-NIDC) are interesting for their potential nonlinear response.

Spectral and structural studies of hydrated and anhydrous crystals of potassium *L*-2-nitrimino-1,3-diazepane-4-carbocylate have succeeded in assigning characteristic absorptions bands to functional groups.

The second-harmonic generation activities of hydrated and anhydrous crystals of potassium *L*-2-nitrimino-1,3-diazepane-4-carboxylate have been explained in terms of the crystals' structural peculiarities.

The thermal properties of hydrated and anhydrous crystals of potassium *L*-2-nitrimino-1,3-diazepane-4-carboxylate have also been studied.

2. Experimental

L-nitroarginine was used as the initial reagent, and was obtained by direct nitration of powder *L*-arginine («Sigma Aldrich,» [linear formula – H$_2$NC(=NH)NH(CH$_2$)$_3$CH(NH$_2$)CO$_2$H, molecular weight – 174.20, ≥98 %, TLC, form – powder, color – white, melt point – 222 °C, solubility – H$_2$O:50 mg/ml]) [11]. From a water solution of 1:1 molar ratio made of *L*-nitroarginine and MOH, M*L*-2-nitrimino-1,3-diazepane-4-carboxylate metallic salts (M(*L*-NIDC)·H$_2$O) were crystallized at room temperature via slow evaporation. The infrared spectra of the metallic salts of these anhydrous compounds were obtained by dehydration.

Attenuated total reflection Fourier transform infrared (FT-IR ATR) spectra were registered using a Nicolet Nexus FT-IR spectrometer equipped with a ZnSe prism (4000…650 cm^{-1}, single reflection accessory, corrected ATR distortion, number of scans: 32, resolution: 4 cm^{-1}). Fourier-transform Raman spectra were registered using NXP FT-Raman Module of Nicolet 5700 spectrometer (Nd: YVO$_4$ laser with 976 nm wavelength, Happ-Genzel anodization, 4000…200 cm^{-1}, resolution: 4 cm^{-1}, power at the sample: 0.02 W, number of scans: 1024). The same spectrometer was used for measuring IR spectra with

a Nujol mull (650…400 cm^{-1}, resolution: 2 cm^{-1}, number of scans: 32).

Thermal properties have been studied in the temperature range 20–500 °C using a Paulik-Erdey type derivatograph (MOM, Hungary). For the study of K(*L*-NIDC)·H$_2$O crystals, a sample with mass of 96 mg was used and was heated at a rate of 5°/min. For K(*L*-NIDC) crystals, the sample had mass of 100.5 mg and was heated at the rate of 5°/min.

Tests with a Boethius-type microscope equipped with a heating stage were performed in the temperature range of 20…350 °C.

For the evaluation of SHG activity, a modified version of the powder method [12] was used (Q-switching Nd: YAG pulse laser (20 ns pulse duration and 8Hz frequency) with wavelength λ=1.064 μm).

3. Results and Discussion

3.1. Crystal structure

In a strong alkaline medium (MOH (M=K,Na,Li), *L*-nitroarginine transforms into the cycled form of *L*-nitroarginine (*L*-2-nitrimino-1,3-diazepane-4-carboxylic acid (*L*-NIDCA)) at room temperature in a water solution. The carboxylic group acquires a negative charge after losing a proton ((*L*-NIDC)$^-$), and the forms an ionic bond with a metallic cation (M$^+$(*L*-NIDC)$^-$). For the sake of convenience, let's consider some important peculiarities of the crystal and molecular structure of K(*L*-NIDC)·H$_2$O (Fig. 1) [10].
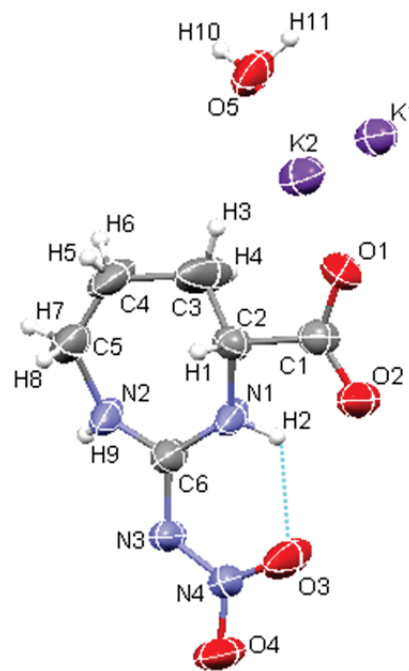

Fig. 1. *Molecular structure of the K (L-NIDC)·H$_2$O crystal*

In the K(*L*-NIDC)·H$_2$O crystal structure, the nitro group is included into N1-H2···O3 type intramolecular hydrogen bonds at distances of N···O 2.560(6) Å.

Similar intramolecular hydrogen bonds are present in the structures of *L*-nitroarginine, the associated salts, and *L*-2-nitrimino-1,3-diazepane-4-carboxylic acid. The water molecule forms into O-H···O type-two hydrogen bonds with neighboring molecule's carboxylate group with the O···O distance of (O5-H11···O1) 2.883(6) Å and with the nearest nitro group with the O···O distance of (O5-H10···O3) 2.799(5) Å. Two potassium cations in the structure are in special positions, on a twofold axis. The atoms of the diazepane cycle are located in different planes, which can be seen at the torsion angles of C6-N1-C2-C3=–67.3(14)° and C6-N2-C5-C4=53.5(15)° torsion angles. The same pattern appears in the cases of *L*-NIDCA·H$_2$O, *L*-NIDCA crystals [6, 7].

3.2. Thermal properties

The process of dehydration and the thermal properties of the K(*L*-NIDC)·H$_2$O crystal (Fig. 2) were also addressed in our study. In the thermogravimetric curve, we can see that along with the increase in temperature the absorbed humidity desorbs at first, and then the main process of dehydration takes place from 97 up to 126 °C. From the differential thermal analysis (DTA) curve, we can see that the dehydration process is endothermic, as expected. The TG curve shows that the total dehydration is 6 % of the sample mass, which corresponds to the calculated value (6.9 %). Tests of the thermal properties using a heating-stage microscope showed that the dehydration process starts at 104 °C and further heating decomposes the substance.
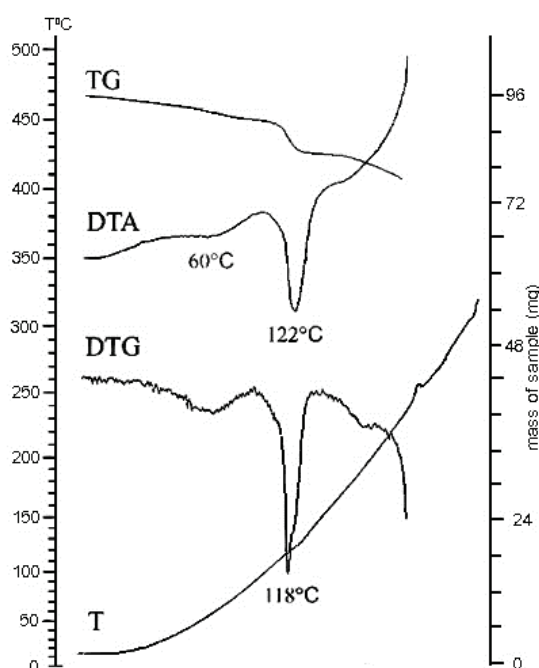

Fig. 2. *Thermogravimetric (TG), derivative thermogravimetric (DTG) and differential thermal analysis (DTA) curves of the K(L-NIDC)·H$_2$O*

3.3. Vibrational spectra of K(*L*-NIDC)·H$_2$O and K (*L*-NIDC)

The infrared (IR) absorption and Raman spectra of K(*L*-NIDC)·H$_2$O and K(*L*-NIDC) crystals are shown in Fig. 3 and 4. The wavenumbers of peaks and their assignments are listed in Table 1. The stretching ν(OH) vibrations of the water molecule are in the 3488–3362 cm^{-1} range. Water molecules forms O5-H11···O1 and O5-H10···O3 hydrogen bonds with O···O distances of 2,883(6) Å and 2.799(5) Å respectively. The expected values of ν(OH) for these O···O distances are 3490 and 3300 cm^{-1} [13], which correspond well with the observed values. We assign the intensive absorption bands with peaks at 3484 and 3362 cm^{-1} and weakly expressed 3488 and 3381 cm^{-1} Raman lines to ν(OH) stretching vibrations, which are absent in the IR and Raman spectra of the K(*L*-NIDC) crystal. By comparing the IR and Raman spectra of K(*L*-NIDC)·H$_2$O and K(*L*-NIDC) crystals, we assign the absorption band with a peak at 1656 cm^{-1} to δ(HOH) deformation vibration of the water molecule. We reach this conclusion if we explore the spectra of the K(*L*-NIDC)·H$_2$O crystal before dehydration and after dehydration at 150 °C.

The characteristic absorption bands and Raman lines of the N1-H2 and N2-H9 bonds in the case of K(*L*-NIDC)·H$_2$O correspond to absorption bands at 3253 and 3149 cm^{-1} and Raman lines at 3252 and 3145 cm^{-1}. The case of K(*L*-NIDC) gives 3236 and 3125 cm^{-1} absorption bands and a 3280 cm^{-1} Raman line. As a rule, the ν(CH) stretching vibrations of the CH and CH$_2$ groups are expressed through intense lines in the Raman spectrum, unlike the IR spectrum. Therefore, the Raman lines in the 2992–2870 cm^{-1} (Fig. 3) and 2998–2863 cm^{-1} (Fig. 4) ranges and the respective absorption bands are assigned to stretching vibrations of the C-H bonds.

In the IR and Raman spectra we assign the well-expressed 1618 and 1606 cm^{-1} absorption bands and the weakly expressed 1614 and 1601 cm^{-1} Raman lines to the stretching vibrations of the carboxylate group in the cases of K(*L*-NIDC)·H$_2$O and K(*L*-NIDC) crystals.

In the IR spectrum, the asymmetric and symmetric stretching vibrations (ν_{as}(NO$_2$) and ν_s(NO$_2$)) of the nitro group, characterized by absorption bands, are relatively intense. In the Raman spectrum, however, the relatively intense lines characterize the symmetric stretching vibrations of the nitro group [14, 16]. Often, the absorption band in the IR spectrum that characterizes the symmetric stretching vibrations of the nitro group is split into two bands near 1300–1360 cm^{-1} [14]. In cyclic nitro compounds, if the nitro group is linked to a ring with a–N-NO$_2$ type bond, then ν_{as}(NO$_2$) vibrations are in the
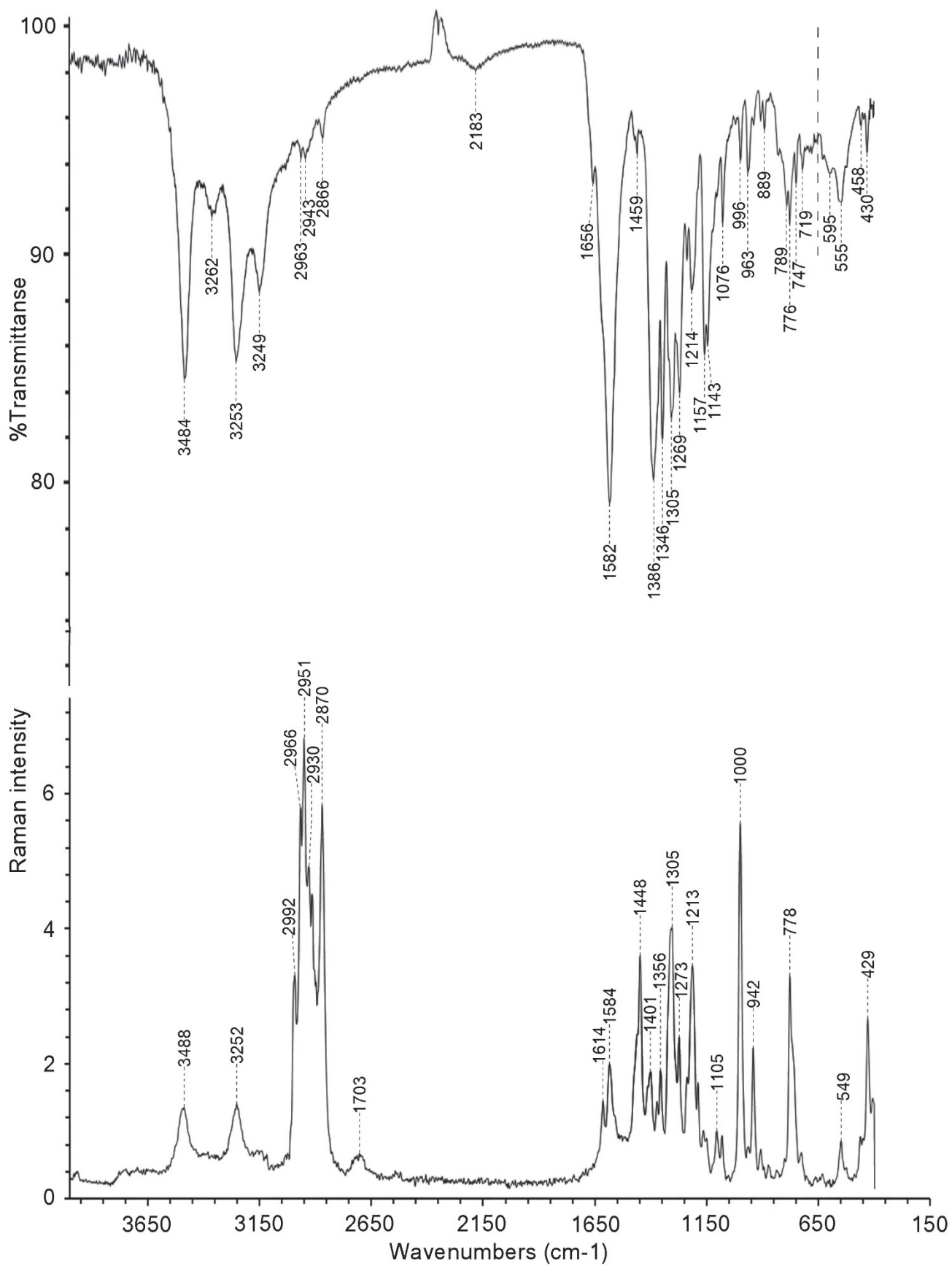
Fig. 3. *Infrared (b) and Raman (a) spectra of the K(L-NIDC)·H₂O crystal*

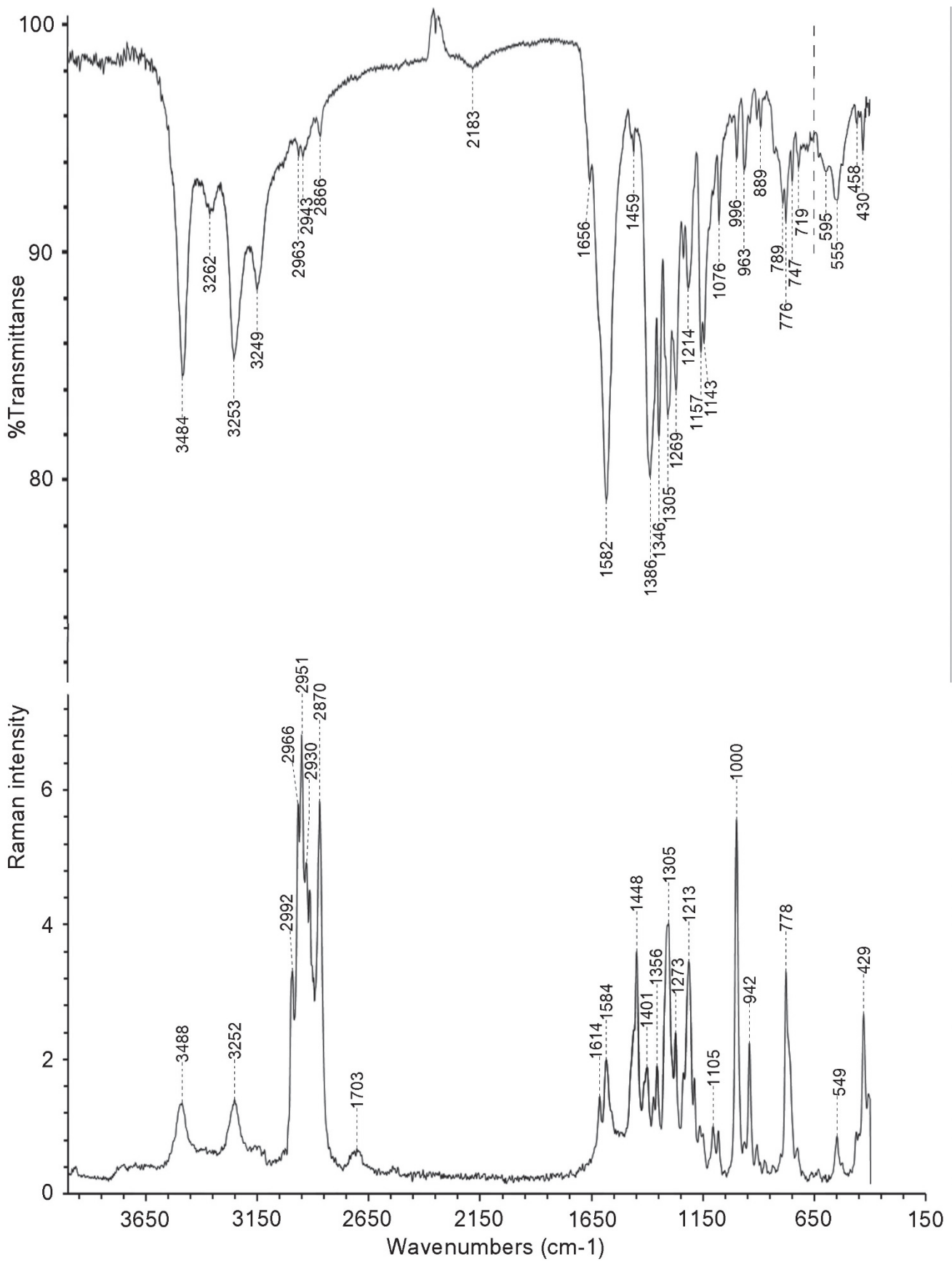*Fig. 4.* Infrared (b) and Raman (a) spectra of the K(L-NIDC) crystal

1540–1590 cm⁻¹ range and $\nu_s(NO_2)$ vibrations are in the 1250–1320 cm⁻¹ range.

Based on these findings, we assign $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ stretching vibrations of the nitro group to 1582, 1307 and 1298 cm⁻¹ absorption bands in the case of K(L-NIDC) and to 1582, 1318 and 1305 cm⁻¹ in the case of K(L-NIDC)·H$_2$O crystals and to the lines in the Raman spectrum at 1569, 1307 and 1295 cm⁻¹ for the K(L-NIDC) crystal and to the Raman lines 1584, 1309 and 1305 cm⁻¹ for the K(L-NIDC)·H$_2$O crystal.

The deformation vibrations of the nitro group ($\delta(NO_2)$) in the IR spectrum are well-expressed, but they are not often expressed in the Raman spectrum, so we assign the absorption band with a peak at 826 cm⁻¹ to $\delta(NO_2)$ vibrations for K(L-NIDC)·H$_2$O and the absorption line at 827 cm⁻¹ for the K(L-NIDC) crystal.

3.4. Relation between nonlinear activity and crystal structure

Crystals that contain an acceptor nitro group (NO$_2$) and a donor amino group (NH$_2$) may possess strong NLO properties. Some monohydrate compounds also have strong NLO properties [17]. Evaluation of SHG intensities showed that the K(LNIDC) crystal demonstrates the expected high-intensity SHG (2.75 times that of KDP), while the K(L-NIDC)·H$_2$O crystal exhibits low SHG intensity (four times less that of KDP).

Table 1. *Wavenumbers (in cm⁻¹) and assignment of peaks in IR and Raman spectra of K(L-NIDC)·H$_2$O and K(L-NIDC)*

K(L-NIDC)·H$_2$O		K(L-NIDC)		Assignment
IR	Raman	IR	Raman	
3484, 3362	3488, 3381			ν(OH), H$_2$O
3253, 3149	3252, 3145	3236, 3125	3280	NH, ν(NH)
3032, 2963, 2943, 2866	2992, 2966, 2951, 2930, 2915, 2870, 2714, 2703	2991, 2939, 2861	2998, 2945, 2929, 2915, 2897, 2889, 2876, 2869, 2863, 2734, 2720	CH, CH$_2$, ν(CH)
2183		2209		combi
1656				δ(HOH)
1618sh	1614	1606	1601	ν_{as}(COO⁻)
1582	1584	1582	1569	ν_{as}(NO$_2$)
1471sh, 1459, 1394sh	1563sh, 1461sh, 1448, 1414sh	1457, 1439	1461, 1442	δ(CH$_2$), ω(CH$_2$), τ(CH$_2$)
1386	1401	1374	1385	ν_s(COO⁻)
1366sh, 1346	1372, 1356	1345	1352	
1318sh, 1305	1309, 1305	1307, 1298sh	1307sh, 1295	ν_s(NO2)
1284sh, 1269, 1236, 1214,1157, 1143,1118sh, 1101	1273, 1238, 1214, 1189, 1165, 1149, 1105	1278, 1258, 1236, 1206, 1192sh,1157	1276sh, 1235, 1215, 1195sh, 1163	ρ(CH$_2$), ν(C-N)
1076	1081	1093, 1068	1094, 1078	
1018, 996	1000	1001sh, 989	992	
963, 937	964, 942	960, 938	963, 957, 936	
906	908	910	915	
889	894, 874	885	901, 887	
826		827sh		δ(NO$_2$)
789	837, 802	809	811	
776	778			
		788sh, 781, 766	770	
747	762sh	743	736	
719	726	7173	713	
629				
	632	657, 628, 598,		
544, 522				
557, 537				
595				ν_L(HOH)
555	549	460		
523, 458, 446	462	443, 431, 407, 404	458, 414	
430	429, 407		364, 305, 268, 208	

ν – stretching; δ – deformation scissoring; ω – wagging; τ – twisting; ρ – rocking; γ – out-of-plane bending; s – symmetric; as – asymmetric; sh – shoulder; combi – combinational; overtones; ν_L – vibration.
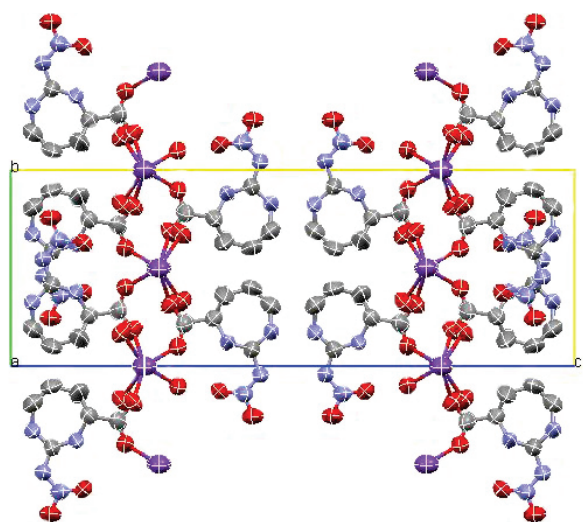
Fig. 5. *The crystal structure of K(L-NIDC)·H₂O (projection on a axis is shown)*

The low SHG intensity of the K(L-NIDC)·H$_2$O crystal is explained by the features of its structure. Despite its lack of centrosymmetry, the structure can be thought of as pseudo-centrosymmetric [15]. Determination of the crystal structure showed that the K(L-NIDC)·H$_2$O crystal has an orthorhombic non-centrosymmetric $I222$ space group with eight molecules (K$^+$(L-NIDC)$^-$) in the unit cell (Fig. 5).

In the non-centrosymmetric K(L-NIDC)·H$_2$O crystal, the positioning of these eight molecules is such that the structure is nearly centrosymmetric (Fig. 5); otherwise it has pseudocentrosymmetry.

The pseudocentrosymmetric structure in the turn of the crystal explains its low NLO efficiency [15].

4. Conclusions

The physical properties of crystal salts K(L-NIDC)·H$_2$O and K(L-NIDC) obtained from L-nitroarginine derivatives (K(L-NIDC)·H$_2$O) were studied to reveal the influence of crystal and molecular structure on the crystals' nonlinear properties. K(L-NIDC)·H$_2$O and K(L-NIDC) crystal IR and Raman spectra were measured, and considering our focus on the structure, functional groups were a central focus. We found that the K(L-NIDC)·H$_2$O crystal is stable up to 60 °C and possesses pseuodocentrosymmetry, explaining its low NLO transformation efficiency. The K(L-NIDC) crystal is stable up to 97 °C and it may lack pseudocentrosymmetry, explaining its strong NLO properties.

References

[1] Koreneva L.G., Davydov B.V., Zolin V.F. *Nonlinear optics of molecular crystals.* Nauka, Moscow, 1985, 199 p. (in Russian).

[2] Apreyan R.A., Karapetyan H.A., Petrosyan A.M. On molecular structure of *L*-nitroarginine. *J. Mol. Struct*., 2008, vol. 874, no.1–3, pp. 187–193. doi: 10.1016/j.molstruc.2007.04.006

[3] Apreyan R.A., Karapetyan H.A., Petrosyan A.M. Polymorphism of *L*-nitroargininium bromide monohydrate. *J. Mol. Struct*., 2008, vol. 875, no. 1–3, pp. 272–281. doi: 10.1016/j.molstruc.2007.04.043

[4] Apreyan R.A., Fleck M., Atanesyan A.K., Sukiasyan R.P., Petrosyan A.M. *L*-Nitroargininium picrate. *J. Mol. Struct.*, 2015, vol. 1101, pp. 236–242. doi: 10.1016/j.molstruc.2015.08.035

[5] Petrosyan A.M., Ghazaryan V.V., Giester G., Fleck M. Sulfamates and methanesulfonates of L-arginine and L-histidine. *J. Mol. Struct.*, 2018, vol. 1163, pp. 114–127. doi: 10.1016/j.molstruc.2018.02.112

[6] Karapetyan H.A. *L*-2-Nitrimino-1,3-diazepane-4-carboxylic acid. *Acta Cryst*., 2008, vol. 64, no.5, p. o943. doi: 10.1107/S1600536808011835

[7] Karapetyan H.A. *L*-2-Nitrimino-1,3-diazepane-4-carboxylic acid monohydrate. *Acta Cryst.,* 2008, vol. 64, no. 7, p. o1222. doi: 10.1107/S1600536808015146

[8] Paul R., Anderson G.W., Callahan F.M. Some side reactions of nitro-*L*-arginine. *J. Org. Chem.,* 1961, vol. 26, no. 9, pp. 3347–3350. doi: 10.1021/jo01067a078

[9] Mekay A.F., Wright G.F. Preparation and properties of 2-Nitramino-Δ²-1,3-diazacycloalkenes. *J. Am. Chem. Soc.,* 1948, vol. 70, no.1, pp. 430–431. doi: 10.1021/ja01181a525

[10] Karapetyan H.A. Potassium *L*-2-nitrimino-1,3-diazepane-4-carboxylate monohydrate. *Acta Cryst.*, 2008, vol. 64, no.11, p. m1369. doi: 10.1107/S1600536808023817

[11] Hofmann K., Peckham W.D., Rheiner A. Studies on polypeptides. VII. The synthesis of peptides containing arginine. *J. Am. Chem. Soc.,* 1956, vol. 78, no. 1, pp. 238–242. doi: 10.1021/ja01582a065

[12] Rieckhoff K.E., Peticolas W.L. Optical second-harmonic generation in crystalline amino acids. *Science*, 1965, vol. 147, no. 3658, pp. 610–611. doi: 10.1126/science.147.3658.610

[13] Nakamoto K., Margoshes M., Rundle R.E. Stretching frequencies as a function of distances in hydrogen bonds. *J. Am. Chem. Soc.,* 1955, vol. 77, no. 24, pp. 6480–6486. doi: 10.1021/ja01629a013

[14] Mayo D.W., Miller F.A., Hannah R.W. *Course notes on the interpretation of infrared and Raman spectra.* John Wiley & Sons, USA, 2004, 600p.

[15] Suponitsky K.Yu., Timofeeva T.V., Antipin M.Yu. Molecular and crystal design of nonlinear optical organic materials. *Russ. Chem. Rev.*, 2006, vol. 75, no. 6, pp. 457–496. doi: 10.1070/RC2006v075n06ABEH003602

[16] Oyumi Y., Brill T.B., Rheingold A.L. Thermal decomposition of energetic materials. 7. High-rate FTIR studies and the structure of 1,1,1,3,6,8,8,8-octanitro-3,6-diazaoctane. *J. Phys. Chem.,*1985, vol. 89, no. 22, pp. 4824–4828. doi: 10.1021/j100268a033

[17] Petrosyan H.A., Apreyan R.A., Hovhannesyan A.A., Atanesyan A.K., Petrosyan A.M. Nonlinear optical activity and spectroscopy of L-nitrohistidine monohydrate. *J. Contemp. Phys.*, 2009, vol. 44, no. 1, pp. 43–49.