SUPPORTING INFORMATION

Pb₆O₅(NO₃)₂: a Nonlinear Optical Oxynitrate Structurally Based on Lead Oxide Framework

Dmitry O. Charkin,[†] Artem S. Borisov,[‡] Igor V. Plokhikh,[§] Sergey Yu. Stefanovich,[†] Anastasiya I.

Zadoya,[‡] Alexander N. Zaloga,[¶] Tatiana F. Semenova[‡] and Oleg I. Siidra^{*, ‡,||}

[†]Department of Chemistry, Moscow State University, Leninskie Gory 1, 119991 Moscow, Russia [‡]Department of Crystallography, St. Petersburg State University, 199034 St. Petersburg, Russia [§]Institute of Inorganic Chemistry, University of Regensburg, 93053, Regensburg, Germany [¶]Siberian Federal University, Svobodny Prosp. 79/10, Krasnoyarsk 660041 Russia [∥]Kola Science Center, Russian Academy of Sciences, Apatity, Murmansk Region, 184200, Russia Synthesis of $Pb_6O_5(NO_3)_2$. Lead oxide (massicot, Vekton, spectroscopic grade) and lead nitrate (Vekton, analytical grade) were taken in 5:1 molar ratio, thoroughly grinded using agate mortar, placed into silica-jacketed alumina crucibles, evacuated to 5 Pa, sealed and annealed at 350°C for 60 hrs (heat ramp 100°C), after which the furnace was switched off. The sample was twice re-ground, re-sealed, and annealed at 450 (60 hrs) and 475°C (55 hrs), respectively. The brown coloring due to NO₂ vapors observed in the sealed tube when heated had completely vanished upon cooling to room temperature. An off-while powder, with a faint creamy tint, was obtained. This approach is reproducible but works for loadings below 1.5-2 g. Use of larger loadings or direct heating the initial mixtures to 450-550°C result in essential (up to 5%) amounts of Pb₃O₂(NO₃)₂ and unreacted PbO.

The previously reported compound $Pb_3O_2(NO_3)_2$ can be obtained in a similar way by heating 2PbO:Pb(NO₃)₂ mixtures at 350°C with one or two intermediate grindings. For this compound, the synthesis is scalable to 3-5 g.

Elemental analysis. Semi-quantitative electron microprobe analysis (LINK AN-10000 EDS system) revealed no other elements, except Pb, with the atomic number greater than 11 (Na).

NLO Properties. SHG test was performed using the standard Kurtz-Perry powder technique [1]. A Minilite-I Nd:YAG laser operating in Q-switched mode with output frequency of 10 Hz, was the source of λ_{ω} = 1064 nm radiation. Green light of the second harmonic at $\lambda_{2\omega}$ = 532 nm, produced by the sample of **1** and reference sample of α -quartz powder (3-5 μ m) was collected in reflection mode and detected by a photomultiplier tube equipped with a narrow band-pass interference filter. The strongest signal, about 120 times above the standard, was registered under ambient conditions in coarse powders with grain size $L \ge 20 \mu m$, the latter value can be viewed as the maximum coherence length of L_c in **1**. The SHG signal diminishes upon heating and vanishes irreversibly at ~ 500°C (Fig. 2). Observed phenomenon correlates well with the thermal stability data. Particle size dependence of the SHG signal for 1 at ambient conditions (Fig. 2) indicates that the compound is not phase matchable. The coherence length of **1** can be taken from Fig. 2 data as $L_c \simeq 18 \mu m$. Calculated from these data and known SiO₂ characteristics, the mean optical nonlinearity of **1** is $\langle d \rangle = 1.54$ pm/V which is above the common range of 0.35 – 1.4 pm/V typical for nitrates and only slightly below the maximum value of ~1.8 pm/V observed for $Sr_2(OH)_3NO_3$. In this respect, nitrates and carbonates (<d> = 0.5 - 1.5 pm/V) exhibit weaker performances compared to borates wherein the value may reach 2.7 pm/V in case of BaB_2O_4 .

[1] Kurtz S.K., Perry T.T. A Powder Technique for Evaluation of Nonlinear Optical Materials. *J. Appl. Phys.* **1968**, *39*, 3798–3813.

Table S1. Composi	tions suggested for	r lead oxide nitrates	in previous studies.
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Composition and PbO	JCPDS	F ₃₀	Synthesis conditions	Reference
molar fraction in brackets	File No.			
6Pb(NO ₃) ₂ ·4PbO(40)	28-0537	0 (unindexed)	n.a.	[1]
Pb(NO ₃) ₂ ·1.4PbO (58.3)	40-0552	8	Thermal decomposition of «Pb ₂ O(NO ₃) ₂ » at 440°C, composition Pb(NO ₃) ₂ ·1.4PbO derived from TGA data	[2]
Pb(NO ₃) ₂ ·2PbO (66.7)	40-0614	3	Thermal decomposition of «Pb(NO ₃) ₂ ·2PbO·1.5H ₂ O» (identity not confirmed) at 150°C (plateau up to 300°C)	[3]
	-	-	Thermal decomposition of Pb(NO ₃) ₂ at ~350°C; confirmed by the structural study	[1]
Pb(NO₃)₂·2.2PbO (68.8)	40-0553	5	n.a.	[2]
Pb(NO ₃) ₂ ·3PbO (75)	39-0543	3	Precipitation of basic lead nitrate by adding aqueous ammonia to Pb(NO ₃) ₂ solution and drying in air. Chemical composition deduced from quantitative analysis and IR data.	[4]
Pb(NO ₃) ₂ ·5PbO (83.3)	23-1159	0 (unindexed)	Thermal decomposition of $Pb_3O_2(NO_3)_2$ at ~500°C	[1]

[1]. Bataille T., Audebrand N., Boultif A., Louër D. Z. Kristallogr. 2004, 219, 881.

[2]. Garçia-Clavel M.E., Martínez-Lope M.J., Casais-Alvarez M.T., Kilany A.M. *Thermochim. Acta* **1986**, 98, 205-212.

[3]. Garçia-Clavel M.E., Martínez-Lope M.J., Casais-Alvarez M.T., Kilany A.M. *Thermochim. Acta* **1986**, 105, 111-116.

[4]. Garçia-Clavel M.E., Martínez-Lope M.J., Casais-Alvarez M.T., Kilany A.M. Thermochim. Acta 1985, 92, 547-551.

"Pb(N	"Pb(NO₃)₂·PbO"		Pb(NO₃)	2	Pb(NO ₃) ₂ ·2PbO		PbO
(JCPDS	S 40-0551)	(JCP	(JCPDS 36-1462)		(calcul	(calculated according to [5])	
<i>d,</i> Å	1, %	d, Å	hkl	1, %	d, Å	hkl	I, %
9.302	18				9.291	002	93
7.369	8						
7.019	19				7.037	101	84
5.862	7				5.884	102	23
4.548	100	4.534	111	100			
4.223	9				4.221	013	38
4.107	11				4.119	112	44
3.922	34	3.928	200	39			
3.693	5				3.691	113	15
3.520	8	3.513	210	8	3.519	202	14
					3.267	114	27
3.250	16				3.240	203	16
3.173	27				3.174	210	95
					3.129	211	55
3.124	41				3.124	015	100
2 002	26				2.890	115	42
2.002	30 7				2.885	020	73
2.825	7	2 777	220	20	2.825	213	23
2.770	30 7	2.777	220	38	2.755	022	12
2.053	/				2.058	205	27
2.569	5				2.568	116	17
2.396	6				2.401	206	21
2.367	57	2.369	311	77			
2.335	14				2.346	303	24
2 200	0				2.303	311 117	18
2.299	0 20	2 260	222	E 1	2.299	11/	1/
2.204	29 10	2.208	ZZZ	21	1 05 4	225	24
1.963	12				1.954	225	24

Table S2. Indexing the PXRD pattern of " $Pb_2O(NO_3)_2$ " as a two-phase sample.

[5]. Bataille T., Audebrand N., Boultif A., Louër D. Z. Kristallogr. 2004, 219, 881.

Compound name	lead oxide nitrate
Molecular formula	$Pb_6O_5(NO_3)_2$
Sum formula	$Pb_6N_2O_{11}$
Molecular weight (g/mol)	1447.1
Space group	Ima2 (46)
Z	4
a /Å	7.39297(8)
b/Å	15.9983(2)
<i>c</i> /Å	11.03860(13)
V/ų	1305.59(3)
$ ho_{calc}$ / g·cm ⁻³	7.3623
Wavelength / Å	0.35451
R-exp /%	4.5
<i>R</i> -p /%	8.3
R-F² /%	4.8
starting angle (20°)	1.002
final angle (2 <i>0</i> °)	37.914
step width (2 <i>0</i> °)	0.002
no. of variables	63

Table S3. Crystallographic and refinement data for $Pb_6O_5(NO_3)_2$ at room temperature.

Table S4. Atomic coordinates of $Pb_6O_5(NO_3)_2$ at room temperature.

Atom	Wyck.	x/a	y/b	z/c	B/Ų
Pb1	4 <i>a</i>	-1/2	1/2	0.219(4)	0.018(2)
Pb2	4 <i>b</i>	-1⁄4	0.6094(3)	0.508(4)	0.030(2)
Pb3	8 <i>c</i>	-0.0151(4)	0.7410(3)	0.242(4)	0.0177(14)
Pb4	4 <i>b</i>	-3⁄4	0.3656(3)	0.000(4)	0.0174(19)
Pb5	4 <i>b</i>	-3⁄4	0.6166(3)	-0.009(4)	0.025(3)
N1	4 <i>b</i>	-0.106(5)	0.181(3)	0.963(5)	0.0285
N2	4 <i>a</i>	-1⁄4	0.143(7)	0.953(10)	0.0285
01	8 <i>c</i>	-1⁄4	0.066(4)	0.936(6)	0.0285
02	4 <i>b</i>	-3⁄4	0.490(4)	0.095(7)	0.0285
03	4 <i>b</i>	0.038(5)	0.639(3)	0.134(6)	0.0285
04	8 <i>c</i>	-1⁄4	0.763(4)	0.087(6)	0.0285
05	4 <i>b</i>	0	0	0.262(11)	0.0285
06	8 <i>c</i>	-0.111(5)	-0.042(3)	0.207(6)	0.0285
07	4 <i>a</i>	0	0	0.37470	0.0285
08	4 <i>b</i>	-1⁄4	0.72500	0.37117	0.0285

			(-,-		
PbO _n polyhedra and NO ₃ triangles OPb ₄ tetrahe						
Pb1-03	2.30(5) ×2	Pb4-03	2.25(7)	O3-Pb4	2.25(7)	
Pb1-04	2.42(5) ×2	Pb4-05	2.27(7)	O3-Pb1	2.30(5)	
Pb1-02	3.21(6) ×2	Pb4-04	2.59(5) ×2	O3-Pb5	2.33(7)	
		Pb4-08	2.66(2)	<03-Pb>	2.30	
Ph2-05	2 22(7)	Ph4-07	3 16(2) x2			

Table S5. Selected bond distances for Pb₆O₅(NO₃)₂.

Pb1-04	2.42(5) ×2	Pb4-05	2.2/(/)	03-Pb1	2.30(5) ×2
Pb1-02	3.21(6) ×2	Pb4-O4	2.59(5) ×2	O3-Pb5	2.33(7)
		Pb4-08	2.66(2)	<03-Pb>	2.30
Pb2-05	2.22(7)	Pb4-07	3.16(2) ×2		
Pb2-08	2.39(3)			O4-Pb3	2.07(6)
Pb2-06	2.66(7) ×2	Pb5-04	2.25(6) ×2	O4-Pb5	2.25(6)
Pb2-01	2.91(4) ×2	Pb5-03	2.33(7)	O4-Pb1	2.42(5)
Pb2-02	2.92(7)	Pb5-07	2.92(2) ×2	O4-Pb4	2.59(5)
		Pb5-01	3.42(4) ×2	<04-Pb>	2.33
Pb3-04	2.07(6)				
Pb3-08	2.26(3)	N1-01	1.23(7) ×2	O5-Pb2	2.22(7)
Pb3-05	2.46(6)	N1-02	1.24(13)	O5-Pb4	2.27(7)
Pb3-01	2.77(7)			O5-Pb3	2.46(6) ×2
Pb3-01	3.44(7)	N2-06	1.22(8) ×2	<05-Pb>	2.35
		N2-07	1.25 (13)		
				08-Pb3	2.26(3) ×2
				08-Pb2	2.39(3)
				08-Pb4	2.66(2)
				<08-Pb>	2.39

Table S6. Bond valence sums for $Pb_6O_5(NO_3)_2$.

	01	02	03	04	05	06	07	08	Σ
Pb1		0.08×2↓→	0.5×2↓→	0.39×2→					1.95
Pb2	0.14×2→	0.14			0.59	0.24×2→		0.42	1.92
Pb3	0.05			0.80	0.36×2↓			0.55×2↓	1.95
	0.19								
Pb4			0.56	0.28×2→	0.53		0.09×2↓→	0.24	2.06
Pb5	0.05×2→		0.47	0.56×2→			0.14×2 \downarrow \rightarrow		1.97
N1	1.73×2→	1.68							5.13
N2						1.77×2→	1.64		5.18
Σ	2.16	1.98	2.03	2.03	1.84	2.01	2.1	1.76	

Parameters for Pb-O: Krivovichev S.V., Brown I.D. Are the compressive effects of encapsulation an artefact of the bond valence parameters? // Zeitschrift für Kristallographie, 2001, 216, 245-247.

Parameters for N-O: Brese N.E., O'Keeffe M. Bond-valence parameters for solids // Acta Crystallographica, 1991, B47, 192-197.



Figure S1. Pure powder sample of $Pb_6O_5(NO_3)_2$.



Figure S2. Rietveld refinement plot for Pb₆O₅(NO₃)₂.

IR studies. IR spectrum of **1** (Fig. S3, Table S7) was registered on a Bruker Vertex 70 FTIR spectrometer. 3 mg of the sample were carefully ground with 200 mg of preliminary dehydrated potassium bromide and pressed into pellet; the reference sample was pure KBr.



Figure S3. Infrared (FTIR) spectrum of Pb₆O₅(NO₃)₂.

No.	Intensity	Wavenumber	Assignment
1	S	1383	v ₃ (NO ₃)
2	S	1291	v ₃ (NO ₃)
3	m	1040	v1 (NO3)
4	m	808	v ₂ (NO ₃)
5	m	487	Pb-O
6	m	457	Pb-O

Table S7. Tentative assignment [6] of bands in the IR spectrum of Pb₆O₅(NO₃)₂.

[6] Bon, A.M., Benoit, C., Bernard, O. Dynamical properties of crystals of Sr(NO₃)₂, Ba(NO₃)₂, and Pb(NO₃)₂. I. Infrared spectra and structure. *Phys. Stat. Solidi* B 1976, 78, 67-78.

Thermal analysis. The TG/DSC curves for **1** (Fig. S4) were registered on a Netzsch STA 449 F3 thermal analyzer. A 100.365 mg sample was placed in an alumina crucible and heated in argon atmosphere within the temperature range of 31– 700 °C (heating rate 10°C/min, argon flow 20 ml/min). The DSC curve exhibits a weak endothermic peak at ~140°C most likely due to removal of surface absorbed water. The second strong endothermic effect at ~560°C corresponds to the decomposition. Thermal behavior is in good agreement with HT X-ray.



Figure S4. TG and DSC curves for $Pb_6O_5(NO_3)_2$.

HT X-ray diffraction. High temperature PXRD studies were performed on a Rigaku Ultima diffractometer. In the 25-200°C range, the temperature increment was 25°C, within 200 – 600°C, 15°C. The decomposition starts at 450°C with intermediate formation of Pb₃O₄ along with low-temperature α-PbO (litharge); the final decomposition product is β-PbO (massicot) (Fig. S5). The decomposition onset temperature is lower than that registered in DTA study as the sample was heated with essentially lower rate, i.e. more close to the equilibrium conditions. Note that in a closed system, *e.g.* in a sealed silica capsule during the synthesis, **1** is stable at least until 550°C.

The evolution of unit cell parameters with temperature is shown in Figure S6. No effect is observed until 425-450°C which may be considered as decomposition point of **1** in an open system. The calculations of the unit cell parameters were performed using the Jana 2006 software. TEV (Thermal Expansion Visualizing) software [7] was used for determination of the thermal expansion tensor from diffraction data.

The temperature dependencies of the unit cell parameters of $Pb_6O_5(NO_3)_2$ were described in the temperature range of $25 - 450^{\circ}$ C by a linear polynomial function:

 $a(T) = 7.355(1) + 2.771 \times 10^{-4}T \text{ Å}$ $b(T) = 16.04(1) + 2.966 \times 10^{-4} \text{ T}\text{ Å}$

 $c(T) = 11.062(1) + 2.061 \times 10^{-4} TÅ$

No evidence of temperature induced phase transition was observed. $Pb_6O_5(NO_3)_2$ expands anisotropically until its decomposition at about 425 degrees.

[7] T. Langreiter & V. Kahlenberg (2015) TEV – a program for the determination and visualization of the thermal expansion tensor from diffraction data. Crystals, 5, 143-153.



Figure S5. Three-dimensional perspective plot showing all diffractograms of $Pb_6O_5(NO_3)_2$ with increasing temperature. The dashed lines indicate the region of decomposition of $Pb_6O_5(NO_3)_2$ into tetragonal and orthorhombic polymorphs of PbO and Pb_3O_4 .



Figure S6. Evolution of unit cell parameters for $Pb_6O_5(NO_3)_2$.



Figure S7. Pole figures of the thermal expansion coefficients of $Pb_6O_5(NO_3)_2$.