Electronic supplementary information

UNVEILING THE CORRELATION BETWEEN STRUCTURAL ORDER-DISORDER CHARACTER AND PHOTOLUMINESCENCE EMISSIONS OF $NANBO_3$

G. F. Teixeira[a], E. Silva Junior[a], A. Z. Simões[b], E. Longo[a], M. A Zaghete[a].

[a]Universidade Estadual Paulista- Unesp- Instituto de Química de Araraquara, Rua Professor Fraancisco Degni 55, Bairro Quitandinha, P.O. Box 355, 14800-900, Araraquara, São Paulo, Brazil, Fone: +55 16 3301-9500; Fax: +55 16 3301-2308.

[b]Universidade Estadual Paulista- Unesp - Faculdade de Engenharia de Guaratingueta, Av. Dr Ariberto Pereira da Cunha 333, Bairro Pedregulho, P.O. Box 355, 12.516-410, Guaratinguetá, São Paulo, Brazil, Phone: +55 12 3123-2765; Fax: +55 12 3123-2800

*corresponding author: mina.guilher@gmail.com

A. NbO_6 parameters from Rietveld refiment

Table S1. Bond lengths (Nb-O), bond angles variance, polyhedral volume and coordination number of [NbO_6] octahedron of $NaNbO_3$ (CIF ICSD n°97669).

$NaNbO_3$ (CIF ICSD n° 97669) – *Pbma*-orthorhombic			
Bond length (Nb-O) (Å)			
[NbO_6]#1	**[NbO_6]#2**	**[NbO_6]#3**	**[NbO_6]#4**
(Nb1-O3) = 2.0854Å	(Nb1-O3) = 2.0854 Å	(Nb1-O3) = 2.0854 Å	(Nb1-O3) = 2.0854 Å
(Nb1-O2) = 1.9634 Å	(Nb1-O4) = 1.9436 Å	(Nb1-O1) = 1.9924 Å	(Nb1-O4) = 1.9436 Å
(Nb1-O4) = 1.9436 Å	(Nb1-O2) = 1.9634 Å	(Nb1-O4) = 1.9436 Å	(Nb1-O1) = 1.9924 Å
(Nb1-O1) = 1.9924 Å	(Nb1-O3) = 1.9675 Å	(Nb1-O2) = 1.9634 Å	(Nb1-O3) = 1.9675 Å
(Nb1-O4) = 1.9816 Å	(Nb1-O1) = 1.9924 Å	(Nb1-O4) = 1.9816 Å	(Nb1-O2) = 1.9634 Å
(Nb1-O3) = 1.9675 Å	(Nb1-O4) = 1.9816 Å	(Nb1-O3) = 1.9675 Å	(Nb1-O4) = 1.9816 Å
Average Bond length (Å)			
1.9885	1.9885	1.9885	1.9885
Polyhedral volume ($Å^3$)			
10.4112	10.4112	10.4112	10.4112
Distortion index (bond length)			
0.01672	0.01672	0.01672	0.01672
Bond angle variance (deg^3)			
15.4624	15.4624	15.4624	15.4624
Effective coordination number			
5.8886	5.8886	5.8886	5.8886
[NbO_6]#5	**[NbO_6]#6**	**[NbO_6]#7**	**[NbO_6]#8**
(Nb1-O4) = 1.9816 Å	(Nb1-O3) = 1.9675Å	(Nb1-O4) = 1.9816 Å	(Nb1-O3) = 1.9675 Å
(Nb1-O2) = 1.9634 Å	(Nb1-O4) = 1.9816 Å	(Nb1-O1) = 1.9924 Å	(Nb1-O4) = 1.9816 Å
(Nb1-O3) = 1.9675 Å	(Nb1-O2) = 1.9634 Å	(Nb1-O3) = 1.9675 Å	(Nb1-O1) = 1.9924 Å
(Nb1-O1) = 1.9924 Å	(Nb1-O4) = 1.9436 Å	(Nb1-O2) = 1.9634 Å	(Nb1-O4) = 1.9436 Å
(Nb1-O4) = 1.9436 Å	(Nb1-O1) = 1.9924 Å	(Nb1-O4) = 1.9436 Å	(Nb1-O2) = 1.9634 Å
(Nb1-O3) = 2.0854 Å	(Nb1-O3) = 2.08541 Å	(Nb1-O3) = 2.0854 Å	(Nb1-O3) = 2.0854 Å
Average Bond length (Å)			
1.9885	1.9885	1.9885	1.9885
Polyhedral volume ($Å^3$)			
10.4112	10.4112	10.4112	10.4112
Distortion index (bond length)			
0.01672	0.01672	0.01672	0.01672
Bond angle variance (deg^3)			
15.4624	15.4624	15.4624	15.4624
Effective coordination number			
5.8886	5.8886	5.8886	5.8886

Table S2. Bond lengths (Nb-O), bond angles variance, polyhedral volume and coordination number of $[NbO_6]$ octahedron of $NaNbO_3$ processed in 30 minutes at 180 °C from MAH method.

$NaNbO_3$ (30 minutes) – *Pbma*-orthorhombic			
Bond length (Nb-O) (Å)			
$[NbO_6]$#1	**$[NbO_6]$#2**	**$[NbO_6]$#3**	**$[NbO_6]$#4**
(Nb1-O3) = 2.02072 Å	(Nb1-O3) = 2.02072 Å	(Nb1-O3) = 2.02071 Å	(Nb1-O3) = 2.02071 Å
(Nb1-O2) = 1.96722 Å	(Nb1-O4) = 1.94637 Å	(Nb1-O1) = 1.98618 Å	(Nb1-O4) = 1.94637Å
(Nb1-O4) = 1.94637 Å	(Nb1-O2) = 1.96722 Å	(Nb1-O4) = 1.94637 Å	(Nb1-O1) = 1.98618 Å
(Nb1-O1) = 1.98618 Å	(Nb1-O3) = 1.94386 Å	(Nb1-O2) = 1.96722 Å	(Nb1-O3) = 1.94386 Å
(Nb1-O4) = 2.04229 Å	(Nb1-O1) = 1.98618 Å	(Nb1-O4) = 2.04229 Å	(Nb1-O2) = 1.96722 Å
(Nb1-O3) = 1.94386 Å	(Nb1-O4) = 2.04229 Å	(Nb1-O3) = 1.94386 Å	(Nb1-O4) = 2.04229 Å
Average Bond length (Å)			
1.9844	1.9844	1.9844	1.9844
Polyhedral volume ($Å^3$)			
10.3910	10.3910	10.3910	10.3910
Distortion index (bond length)			
0.01610	0.01610	0.01610	0.01610
Bond angle variance (deg^3)			
5.4291	5.4291	5.4291	5.4291
Effective coordination number			
5.9246	5.9246	5.9246	5.9246
$[NbO_6]$#5	**$[NbO_6]$#6**	**$[NbO_6]$#7**	**$[NbO_6]$#8**
(Nb1-O4) = 2.04229 Å	(Nb1-O3) = 1.94386 Å	(Nb1-O4) = 2.04229 Å	(Nb1-O3) = 1.94386 Å
(Nb1-O2) = 1.966722 Å	(Nb1-O4) = 2.04229 Å	(Nb1-O1) = 1.98618 Å	(Nb1-O4) = 2.04229 Å
(Nb1-O3) = 1.94386 Å	(Nb1-O2) = 1.96722 Å	(Nb1-O3) = 1.94386Å	(Nb1-O1) = 1.98618 Å
(Nb1-O1) = 1.98618 Å	(Nb1-O4) = 1.94637 Å	(Nb1-O2) = 1.96722 Å	(Nb1-O4) = 1.94637 Å
(Nb1-O4) = 1.94637 Å	(Nb1-O1) = 1.98618 Å	(Nb1-O4) = 1.94637 Å	(Nb1-O2) = 1.96722 Å
(Nb1-O3) = 2.02072 Å	(Nb1-O3) = 2.02072 Å	(Nb1-O3) = 2.02072 Å	(Nb1-O3) = 2.02072 Å
Average Bond length (Å)			
1.9844	1.9844	1.9844	1.9844
Polyhedral volume ($Å^3$)			
10.3910	10.3910	10.3910	10.3910
Distortion index (bond length)			
0.01610	0.01610	0.01610	0.01610
Bond angle variance (deg^3)			
5.4291	5.4291	5.4291	5.4291
Effective coordination number			
5.9246	5.9246	5.9246	5.9246

Table S3. Bond lengths (Nb-O), bond angles variance, polyhedral volume and coordination number of $[NbO_6]$ octahedron of the $NaNbO_3$ processed by 60 minutes at 180 °C from MAH method.

$NaNbO_3$ (60 minutes) – *Pbma*-orthorhombic)			
Bond length (Nb-O) (Å)			
$[NbO_6]$#1	**$[NbO_6]$#2**	**$[NbO_6]$#3**	**$[NbO_6]$#4**
(Nb1-O3) = 2.02641Å	(Nb1-O3) = 2.02651 Å	(Nb1-O3) = 2.02641 Å	(Nb1-O3) = 2.02641 Å
(Nb1-O2) = 1.99484 Å	(Nb1-O4) = 1.95105 Å	(Nb1-O1) = 1.95397 Å	(Nb1-O4) = 1.95105 Å
(Nb1-O4) = 1.95105 Å	(Nb1-O3) = 1.99001 Å	(Nb1-O4) = 1.95105 Å	(Nb1-O1) = 1.95397 Å
(Nb1-O1) = 1.95396 Å	(Nb1-O2) = 1.99484 Å	(Nb1-O2) = 1.99484 Å	(Nb1-O3) = 1.99001 Å
(Nb1-O3) = 1.99001 Å	(Nb1-O1) = 1.95396 Å	(Nb1-O4) = 2.00568 Å	(Nb1-O2) = 1.99484 Å
(Nb1-O4) = 2.00568 Å	(Nb1-O4) = 2.00568 Å	(Nb1-O3) = 1.99001 Å	(Nb1-O4) = 2.00568 Å
Average Bond length (Å)			
1.9870	1.9870	1.9870	1.9870
Polyhedral volume (Å^3)			
10.4127	10.4127	10.4127	10.4127
Distortion index (bond length)			
0.01157	0.01157	0.01157	0.01157
Bond angle variance (deg^3)			
10.5047	10.5047	10.5047	10.5047
Effective coordination number			
5.9591	5.9591	5.9591	5.9591
$[NbO_6]$#5	**$[NbO_6]$#6**	**$[NbO_6]$#7**	**$[NbO_6]$#8**
(Nb1-O4) = 2.00568 Å	(Nb1-O3) = 1.99001 Å	(Nb1-O4) = 2.00568 Å	(Nb1-O4) = 2.00568 Å
(Nb1-O2) = 1.99484 Å	(Nb1-O4) = 2.00568 Å	(Nb1-O1) = 1.95386 Å	(Nb1-O3) = 1.99001 Å
(Nb1-O3) = 1.99001 Å	(Nb1-O2) = 1.99484 Å	(Nb1-O2) = 1.99484 Å	(Nb1-O1) = 1.95396 Å
(Nb1-O1) = 1.95386 Å	(Nb1-O4) = 1.95105 Å	(Nb1-O3) = 1.99001 Å	(Nb1-O4) = 1.95015 Å
(Nb1-O4) = 1.95105 Å	(Nb1-O1) = 1.95396 Å	(Nb1-O4) = 1.95105 Å	(Nb1-O2) = 1.99484 Å
(Nb1-O3) = 2.02641 Å	(Nb1-O3) = 2.02641 Å	(Nb1-O3) = 2.02641 Å	(Nb1-O3) = 2.02641 Å
Average Bond length (Å)			
1.9870	1.9870	1.9870	1.9870
Polyhedral volume (Å^3)			
10.4127	10.4127	10.4127	10.4127
Distortion index (bond length)			
0.01157	0.01157	0.01157	0.01157
Bond angle variance (deg^3)			
10.5047	10.5047	10.5047	10.5047
Effective coordination number			
5.9591	5.9591	5.9591	5.9591

Table S4. Bond lengths (Nb-O), bond angles variance, polyhedral volume and coordination number of $[NbO_6]$ octahedron of the $NaNbO_3$ processed in 90 minutes at 180 °C from MAH method.

$NaNbO_3$ (90 minutes) – *Pbma*-orthorhombic			
Bond length (Nb-O) (Å)			
$[NbO_6]$#1	**$[NbO_6]$#2**	**$[NbO_6]$#3**	**$[NbO_6]$#4**
(Nb1-O3) = 2.09413 Å	(Nb1-O3) = 2.09413 Å	(Nb1-O3) = 2.09413 Å	(Nb1-O3) = 2.09413 Å
(Nb1-O2) = 1.98119 Å	(Nb1-O4) = 1.95465 Å	(Nb1-O1) = 1.96524 Å	(Nb1-O4) = 1.95465 Å
(Nb1-O4) = 1.95465 Å	(Nb1-O2) = 1.98119 Å	(Nb1-O4) = 1.95465 Å	(Nb1-O1) = 1.96524 Å
(Nb1-O1) = 1.96524 Å	(Nb1-O3) = 1.93238 Å	(Nb1-O2) = 1.98119 Å	(Nb1-O3) = 1.93238 Å
(Nb1-O4) = 1.98274 Å	(Nb1-O1) = 1.96524 Å	(Nb1-O4) = 1.98274 Å	(Nb1-O2) = 1.99119 Å
(Nb1-O3) = 1.93238 Å	(Nb1-O4) = 1.98274 Å	(Nb1-O3) = 1.93238 Å	(Nb1-O4) = 1.98274 Å
Average Bond length (Å)			
1.9851	1.9851	1.9851	1.9851
Polyhedral volume (Å^3)			
10.3979	10.3979	10.3979	10.3979
Distortion index (bond length)			
0.01832	0.01832	0.01832	0.01832
Bond angle variance (deg^3)			
5.8160	5.8160	5.8160	5.8160
Effective coordination number			
5.8562	5.9246	5.9246	5.9246
$[NbO_6]$#5	**$[NbO_6]$#6**	**$[NbO_6]$#7**	**$[NbO_6]$#8**
(Nb1-O4) = 1.98274 Å	(Nb1-O3) = 1.93238 Å	(Nb1-O4) = 1.98274 Å	(Nb1-O3) = 1.93238 Å
(Nb1-O2) = 1.98119 Å	(Nb1-O4) = 1.98274 Å	(Nb1-O1) = 1.96524 Å	(Nb1-O4) = 1.98274 Å
(Nb1-O3) = 1.93238 Å	(Nb1-O2) = 1.98119 Å	(Nb1-O3) = 1.93238 Å	(Nb1-O1) = 1.96524 Å
(Nb1-O1) = 1.96524 Å	(Nb1-O4) = 1.95465 Å	(Nb1-O2) = 1.98119 Å	(Nb1-O4) = 1.95465 Å
(Nb1-O4) = 1.95465 Å	(Nb1-O1) = 1.96524 Å	(Nb1-O4) = 1.95465 Å	(Nb1-O2) = 1.98119 Å
(Nb1-O3) = 2.09413 Å	(Nb1-O3) = 2.09413 Å	(Nb1-O3) = 2.09413 Å	(Nb1-O3) = 2.09413 Å
Average Bond length (Å)			
1.9851	1.9851	1.9851	1.9851
Polyhedral volume (Å^3)			
10.3979	10.3979	10.3979	10.3979
Distortion index (bond length)			
0.01832	0.01832	0.01832	0.01832
Bond angle variance (deg^3)			
5.8160	5.8160	5.8160	5.8160
Effective coordination number			
5.8562	5.8562	5.8562	5.8562

B. Optical band gap energy (E_{gap})

The optical band gap energy (E_{gap}) was experimentally determinated from Kubelka- Munk method [S1], from UV-vis spectroscopy in diffuse reflectance mode. The line absorption is a result of the states located inside the band gap, and in the parabolic band structure, the absorption coefficient (α) and the E_{gap} of a semiconductor oxide are related through the well-known Equation (1)

$$\alpha h\nu = K\left(h\nu - E_{gap}\right)^{n} \qquad (1)$$

where α is linear absorption coefficient of the material, $h\nu$ is the photon energy, E_{gap} is the optical band gap energy, K is the proportionality constant and n is a constant associated to the different type of electronic transitions, being n = 1/2 for direct allowed transition or n = 2 for indirect allowed transition [S2]. In reflectance diffuse mode, the sample thickness depending of factors related to deep beam penetration such as, package density, particle size and amount of absorbent material in the sample [S3]. The absorption coefficient (α) is related to reflectance (R) by means of equation (2):

$$\alpha = F(R).\left(\frac{s}{2V_r}\right) \qquad (2)$$

where s is the scattering coefficient, V_r is the volumetric fraction of the absorbents species and $F(R)$ is the Kubelka-Munk function [S1], defined by:

$$F(R) = \frac{(1-R)^2}{2R} \cong \frac{k}{s} \qquad (3)$$

where k is the molar absorption coefficient. The coefficients k and s are intrinsic parameters of the material, being that real scattering and absorption coefficients, α_ν and σ_ν and, at given frequency (ν), are related to k and s according:

$$\alpha_\nu = \eta k \qquad (4)$$

$$\sigma_\nu = \chi s \qquad (5)$$

The χ and η values are taken in the limit of the small absorptions, so them admit the values of 1/2 and 4/3, respectively. For small absorption η= 2 and $k = 2\alpha_v$ and the ratio k/s = 0-3 [S3]. Therefore, the Kubelka-Munk function will be:

$$F(R) = \frac{(1-R)^2.\eta}{2R.\chi} = \frac{\alpha_v}{\sigma_v} \qquad (6)$$

Experimentally, the reflectance measured in diffuse mode, the R value in the Kubelka-Munk function will be:

$$R = \frac{R_{sample}}{R_{standard}} \qquad (7)$$

The reflectance measured in (7) assumes that thickness of the sample is infinitely thick and $R_{standard}$ is a material that exhibit absolute reflectance such as, MgO or $\alpha - Al_2O_3$. Lastly, the optical band gap energy will can be calculated from reflectance diffuse mode according:

$$F(R).h\nu = K.\left(h\upsilon - E_{gap}\right)^n \qquad (8)$$

According literature, the electronic transitions allowed for $NaNbO_3$ exhibits an optical absorption spectrum governed by indirect electronic transitions ($n = 2$) between the valence and conduction bands [S4, S5 and S6]. Thus, through of a simple mathematical artifice in the eq. (8) is easy to show that $F(R).h\nu \propto \left(h\nu - E_{gap}\right)^n$ or $[F(R).h\nu]^{1/2} \propto (h\nu - E_{gap})$. Therefore, from UV-vis absorption spectroscopy in diffuse reflectance mode, there is obtained *F(R)* and plotting a graph of $[F(R).h\upsilon]^{1/2}$ versus $h\nu$, admitting that $NaNbO_3$ has an indirect electronic transition (n = 2), it was possible determine of the E_{gap} extrapolating the linear portion of the reflectance curve, plotted with photon energy on the x-axis, in the condition which the reflectance is zero

References

[S1]. P. Kubelka, F. Munk-Aussig, *Zeit. Für. Tech. Phys.*, 1931, **12**, 593.
[S2]. R. A. Smith. *Semiconductors*, 2 ed. London: Cambridge University Press, London; 1978.
[S3]. K. Klier. *J. Opt. Soc. Am*. 1972, **62**, 882.
[S4]. P. Li, H. Xu, L. Liu, T. Kako, N. Umezawa, H. Abe and J. Ye. *J. Mater. Chem. A*, 2014, **2**, 5606.
[S5]. P. Li, S. X. Ouyang, G. C. Xi, T. Kako and J. H. Ye, *J. Phys. Chem. C*, 2012, **116**, 7621.
[S6]. P. Li, S. Ouyang, Y. Zhang, T. Kako and J. Ye, *J. Mater. Chem. A*, 2013, **1**, 1185.