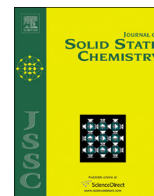




ELSEVIER

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Lithium vanadyl oxalatophosphate: Influence of the water content on the crystal structures and the dehydration scheme

S. Auguste^{a,c}, V. Alonzo^{a,c}, T. Bataille^{b,c}, L. Le Pollès^{a,c}, W. Cañón-Mancisidor^{d,e}, D. Venegas-Yazigi^{d,e}, E. Le Fur^{a,c,*}^a Sciences Chimiques de Rennes, UMR 6226, Ecole Nationale Supérieure de Chimie de Rennes, CNRS, 11 Allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France^b Sciences Chimiques de Rennes, UMR 6226, Université de Rennes 1, CNRS, Campus de Beaulieu, 35042 Rennes Cedex, France^c Université Européenne de Bretagne, 12 avenue Janvier, 35000 Rennes, France^d Facultad de Química y Biología, Universidad de Santiago de Chile, USACH, Casilla, 40 Correo 33, Santiago, Chile^e Centro para el Desarrollo de Nanociencias y Nanotecnología, CEDENNA, Chile

ARTICLE INFO

Article history:

Received 12 June 2013

Received in revised form

18 December 2013

Accepted 21 December 2013

Available online 9 January 2014

Keywords:

Oxalatophosphate

Hydrothermal synthesis

Thermal dependant X-ray diffraction

Solid state NMR

ABSTRACT

Two new lithium vanadyl oxalatophosphites have been synthesized by hydrothermal treatment. The respective formula are $\text{Li}_2(\text{VOHPO}_3)_2\text{C}_2\text{O}_4 \cdot 6\text{H}_2\text{O}$ (**1**) and $\text{Li}_2(\text{VOHPO}_3)_2\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ (**2**). The structures of the compounds have been determined by single crystal X-ray diffraction. Compound **1** crystallizes in triclinic symmetry in space group $P\bar{1}$, $a=6.3592(2)$ Å, $b=8.0789(3)$ Å, $c=9.1692(3)$ Å, $\alpha=64.390(2)$, $\beta=87.277(2)^\circ$, $\gamma=67.624(2)$ and, compound **2** in monoclinic symmetry, space group $P2_1/a$, $a=6.3555(2)$ Å $b=12.6368(7)$ Å $c=9.0242(4)$ Å $\beta=105.167(3)^\circ$. The vanadium phosphite framework consists of infinite chains of corner-sharing vanadium octahedra and hydrogenophosphite tetrahedra. The oxalate groups ensure the connection between the chains. The lithium ions and the water molecules are located between the anionic $[(\text{VO})_2(\text{HPO}_3)_2\text{C}_2\text{O}_4]^{2-}$ layers. Thermal behavior of both compounds was carefully studied by combining thermogravimetric analyses and thermal dependant X-ray diffraction in order to study the thermal stability of the layered oxalatophosphites and to see the influence of the decomposition of the carbon-based anions into the final lithium vanadyl phosphate. Various intermediate phases were evidenced and for both compounds the final product was LiVOPO_4 .

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Vanadium phosphates based compounds have focused great interest during the last decades, due to their various interesting properties, mainly in the field of catalysis [1] but also magnetic behavior [2,3] and porosity [4,5] resulting in a great structural diversity [6]. More recently vanadium phosphate compounds have also been studied as cathodic materials for lithium batteries [7].

The use of carboxylic acids is also well known for the preparation of porous materials [5] and promising results have been obtained for such materials in the area of lithium batteries [8,9]. One of the oldest ligand used in this field is the oxalate ion which can acts as mono-bidentate or bis-bidentate linker resulting in various solids topologies. Hybrid compounds mixing phosphate and oxalate groups have also been described [10–13]. Generally transition metal phosphates are cross-linked by organic groups

resulting in frameworks that can encapsulate various cationic species. In the vanadium oxalatophosphate system, most of the structures described are layered with cationic species and water molecules occluded between the vanadium oxalatophosphate layers [14–18]. Some of these compounds, labeled MOPOF for metal-organic phosphate open frameworks have been very recently tested as materials for lithium batteries [19,20]. They showed reasonable performances in term of ionic mobility and thermal stability that may be improved in the near future with deeper structural studies that can be performed in such materials by combining solid state NMR studies and theoretical calculations [21].

In the course of the preparation of new open structures, the replacement of phosphate by phosphite has been recently proposed, since the $(\text{HPO}_3)^{2-}$ pseudo tetrahedral species have similarities with the phosphate ones $(\text{PO}_4)^{3-}$ but limited connectivity possibilities due to the terminal hydrogen atom connected to phosphorus [22,23]. So far, oxalatophosphites have been little investigated [24–30]. This work deals with the synthesis, the structural study combining X-ray diffraction, ^{31}P , ^7Li MAS NMR and the thermal behavior of two vanadyl oxalatophosphites

* Corresponding author at: Sciences Chimiques de Rennes, UMR 6226, Université de Rennes 1, CNRS, Campus de Beaulieu, 35042 Rennes Cedex, France. Tel.: +33 223 238 016; fax: +33 223 8199.

E-mail address: eric.le-fur@ensc-rennes.fr (E. Le Fur).

incorporating lithium ions. Both compounds present layers, based on vanadium phosphite cross linked by oxalate anions, separated by water molecules and lithium cations in octahedral or tetrahedral coordination depending upon the water content. The complex thermal behavior of the two compounds has been followed by combining thermogravimetric studies and temperature dependent X-ray diffraction. A partially reversible dehydration process is observed. The structure of the intermediate hydrated and anhydrous oxalates are strongly dependent upon the initial water content of the compounds. Finally, the thermal decomposition leads to different forms of LiVOPO_4 for both compounds.

2. Experimental section

2.1. Synthesis

Light green crystals of $\text{Li}_2(\text{VOHPO}_3)_2\text{C}_2\text{O}_4 \cdot 6\text{H}_2\text{O}$ (**1**) have been obtained by hydrothermal treatment. A mixture of V_2O_5 , Li_2CO_3 , H_3PO_3 , $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and H_2O in the molar ratio 1:8:15:2.8:170 was introduced in a 23 mL capacity Teflon-lined stainless steel Parr hydrothermal reaction vessel and heated at 120 °C for 3 days. After slowly being cooled to room temperature, the solid was recovered by vacuum filtration, washed with water, and dried in a desiccant vessel (61.5% yield, calculated with respect to vanadium). Light green crystals of $\text{Li}_2(\text{VOHPO}_3)_2\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ (**2**) have been obtained by the same way, but at 150 °C (38.0% yield).

2.2. X-ray diffraction

The crystal structures of **1** and **2** were determined by single-crystal X-ray diffraction. The experiments were conducted at room temperature using a four-circle Nonius KappaCCD diffractometer, with graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The intensity data collection was performed through the program COLLECT [31]. The compound structure was solved by direct methods (SIR 97 [32]) and refined by the full matrix least-squares procedure based on F^2 , using the SHELXL-97 [33] computer program belonging to the WINGX software package [34].

Crystallographic details for **1** and **2** are given in Table 1. Selected bonds lengths and angles are given in Table 2.

Table 1
Crystal data for **1** and **2**.

	1	2
Formula	$\text{CH}_7\text{LiO}_9\text{PV}$	$\text{CH}_5\text{LiO}_8\text{PV}$
Color; habit	Light green; thin plate	Light green; thin plate
Mr	251.92 g mol ⁻¹	233.90 g mol ⁻¹
Symmetry, space group	Triclinic, <i>P</i> -1	Monoclinic, <i>P</i> ₂ /a
Z	2	4
a	6.3592 (2) Å	6.3555 (2) Å
b	8.0789 (3) Å	12.6368 (7) Å
c	9.1692 (3) Å	9.0242 (4) Å
α	64.390 (2)°	
β	87.277 (2)°	105.167 (3)°
γ	67.624 (2)°	
V	388.92 (2) Å ³	699.52 (5) Å ³
Crystal density	2.151	2.221
μ (mm ⁻¹)	1.502	1.651
Absorption correction:	Multi-scan (SADABS; Shelldrick, 2002)	Multi-scan (SADABS; Shelldrick, 2002)
Number of reflection (> 2 σ)	1789 (1658)	1608 (1232)
R[F ² > 2s(F ²)]	0.046	0.062
wR(F ²)	0.108	0.177
Gof	1.063	1.211

Table 2

Bond distances and possible H-bonds around water molecules in **1** and **2**, as well as their calculated bond valences.

	Distance (Å)	BV ^a
$\text{Li}_2(\text{VOHPO}_3)_2\text{C}_2\text{O}_4 \cdot 6\text{H}_2\text{O}$		
Ow1-Li1	2.02(1)	0.221
Ow1 O6 ⁱ	2.923(5)	0.147
Ow1 O6 ⁱⁱ	3.138(5)	0.109
Ow2-Li1 ⁱⁱⁱ	2.058(8)	0.202
Ow2-Li1 ^{iv}	2.311(8)	0.102
Ow2 O1 ^v	3.060(4)	0.120
Ow2 O2 ^v	2.964(4)	0.138
Ow2 O3 ^{vi}	3.107(4)	0.113
Ow3-Li1 ⁱⁱⁱ	2.061(8)	0.200
Ow3-Li1	2.218(8)	0.131
Ow3 O3 ^{vii}	2.945(4)	0.142
Ow3 O5	2.895(4)	0.154
$\text{Li}_2(\text{VOHPO}_3)_2\text{C}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$		
Ow1-Li1 ^{viii}	1.97(2)	0.256
Ow1-Li1 ^{ix}	2.00(1)	0.236
Ow1 O3 ^v	2.977(7)	0.135
Ow1 O6 ^x	2.899(7)	0.153
Ow2-Li1 ^{xii}	1.87(2)	0.336
Ow2 O1 ⁱⁱⁱ	3.190(8)	0.102
Ow2 O4 ⁱ	3.038(8)	0.123
Ow2 O4 ^{xii}	3.183(8)	0.103

Symmetry codes: (i) 1-x, -y, 2-z; (ii) x, 1+y, -1+z; (iii) 1-x, -y, 1-z; (iv) -1+x, y, z; (v) -x, -y, 2-z; (vi) x, -1+y, z; (vii) 1+x, -1+y, z; (viii) -x, -y, 1-z; (ix) -1/2-x, -1/2+y, 1-z; (x) -1/2+x, -1/2-y, z; (xi) 1/2-x, -1/2+y, 1-z; (xii) x, y, -1+z.

^a Bond valences in italic are calculated according to the formula given in reference [36]: $s = [d(\text{O O})/2.17]^{-8.2} + 0.06$.

The crystal structure of two compounds was also investigated by powder XRD using a Bruker AXS D8 Advance (θ -2 θ Bragg-Brentano geometry) diffractometer working with monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) and equipped with a LynxEye detector. The experiments were performed within the 5–110° 2 θ data range with 2 θ steps of 0.008° and counting time of 1.5 s per step. Rietveld refinements are showed in Appendix Fig. S1.

2.3. Thermal behavior

Coupled thermogravimetric and DSC measurements were performed with a TA instruments SDT Q600 thermobalance under both pure nitrogen and air from room temperature to 850 °C with a heating rate of 0.5 °C/min. Additional DSC measurements were also carried out with a DSC TA Q10 instrument. The powdered samples were introduced in an aluminum crucible and heated at 5 °C min⁻¹ under air to favor the oxidation phenomena during the oxalate decomposition.

Temperature-dependent X-ray diffraction (TDXD) experiments were performed with a powder diffractometer combining the CPS 120 detector from Inel and a high-temperature attachment from Rigaku. An angle of 6° was selected between the incident beam and the surface of the samples. The decompositions of the two compounds were carried out, under flowing air, with a heating rate of 6 °C h⁻¹ from room temperature up to 600 °C. A counting time of 4800 s per pattern was selected for the thermal decomposition of the precursor. Temperature calibration was carried out with standard materials in the actual temperature range.

2.4. NMR spectroscopy

Solid-state NMR spectra were acquired using a Bruker Avance I spectrometer equipped with a 7 T magnet, at Larmor frequencies of 121.65 MHz for ³¹P and 116.68 MHz for ⁷Li. Samples were packed into 2.5-mm outer diameter rotors and rotated at spin

Download English Version:

<https://daneshyari.com/en/article/1329030>

Download Persian Version:

<https://daneshyari.com/article/1329030>

[Daneshyari.com](https://daneshyari.com)