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Ionothermal synthesis and crystal structure of a new layered nickel(II) diphosphate, DRM-1

Ying Wei [a,b], Hermann Gies [c], Zhijian Tian [a,*], Bernd Marler [c], Yunpeng Xu [a], Lei Wang [a], Huaijun Ma [a], Renyan Pei [a,b], Keda Li [a,b], Bingchun Wang [a]

[a] State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China
[b] Graduate University of Chinese Academy of Sciences, Beijing, 100049, China
[c] Institute for Geology, Mineralogy and Geophysics, Ruhr University, Bochum, 44780, Germany

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ABSTRACT

A new layered ammonium nickel(II) diphosphate, $(NH_4)_2[Ni_3(P_2O_7)_2(H_2O)_2]$, has been synthesized ionothermally in the ionic liquid 1-butyl-3-methyl imidazolium bromide and characterized by powder X-ray diffraction, elemental analysis, scaning electron microscopy, thermogravimetry etc. The results of the characterization show that the crystal adopts the monoclinic space group $P2_1/a$ with the lattice constants $a = 9.23529(2)$ Å, $b = 7.98489(2)$ Å, $c = 9.40772(2)$ Å, $\beta = 100.2608(2)°$ and $Z = 2$. Its structure consists of chains of cis- and trans-edge-sharing $[NiO_6]$-octahedra linked via $[P_2O_7]$ units to form layers of $[Ni_3(P_2O_7)_2(H_2O)_2]^{2-}$ in the *ab* plane. Adjacent layers are separated in the *c*-direction by ammonium ions.

Open-framework phosphates of transition metals (Fe, Co, Ni, Mo, Zr etc.) are of great interest because of their structure diversity and the novel features introduced by the transition metals, such as, redox characteristic, optical, electric and magnetic properties etc. [1–3]. Of these materials, the family of nickel phosphates has attracted much attention for the notable properties they exhibit. For example, $Ni_{18}[(HPO_4)_{14}(OH)_3F_9(H_3O/NH_4)_4]\cdot 12H_2O$ (VSB-1) and $Ni_{20}[(OH)_{12}(H_2O)_6]$-$[(HPO_4)_8(PO_4)_4]\cdot 12H_2O$ (VSB-5), composed of edge-sharing $[NiO_6]$- and $[PO_4]$-polyhedra, are well-known because of their high thermal stability, large pore structure, interesting magnetism and active nickel sites in the framework [4,5]. These excellent traits make them promising for the application in the field of gas storage, ion-exchange, selective hydrogenation and base catalysis etc. [4–8].

In the past decades, a series of open-framework nickel phosphates with structures of two- or three-dimensionally linked oxo-polyhedra have been synthesized by using hydrothermal, solvothermal or high-temperature solid state reaction methods [9–14]. The employment of new synthetic techniques has opened up many new possibilities in the exploration of previously unseen materials. Ionothermal synthesis, in which ionic liquids act as solvent and/or template, has been developed in recent years in the preparation of porous materials [15,16]. Noticeably, several new open-framework metallophosphates/phosphites materials have been prepared and structurally analysed using this new approach [17–25]. Herein, we report on the ionothermal synthesis [26] and crystal structure [27] of a new layered nickel diphosphate, $(NH_4)_4[Ni_5(P_2O_7)_4(H_2O)_2]$ denoted as DRM-1 (Dalian Institute of Chemical Physics & Ruhr University Material — one).

After successfully indexing the powder pattern, a structure model of this new diphosphate was developed by comparing the lattice parameters and the whole powder pattern to corresponding data of

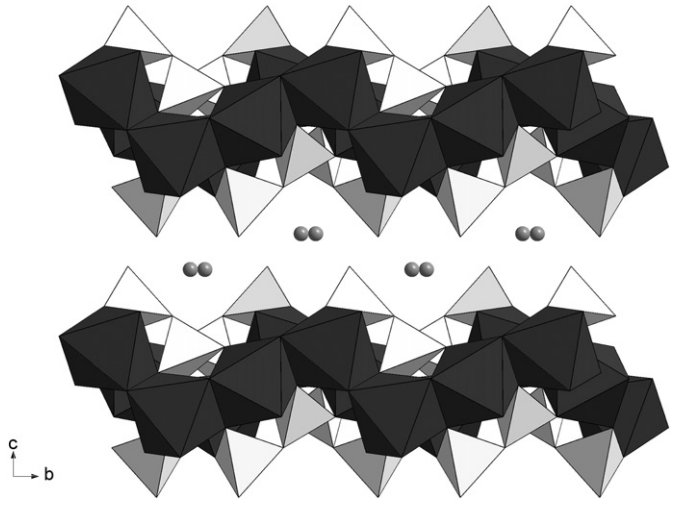

Fig. 1. Polyhedral view of the sturcture of DRM-1 along the *a axis*. ($[NiO_6]$-octahedra, dark-grey; $[PO_4]$-tetrahedra, light-grey; NH^+_4 cations, grey spheres).

* Corresponding author. Tel./fax: +86 411 843 79151.
E-mail address: tianz@dicp.ac.cn (Z. Tian).

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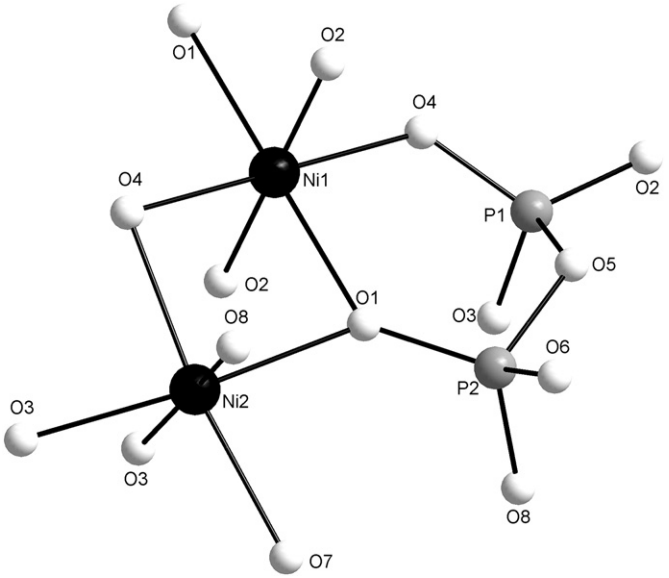

Fig. 2. Local coordination of the framework atoms in DRM-1 showing the atom numbering scheme.

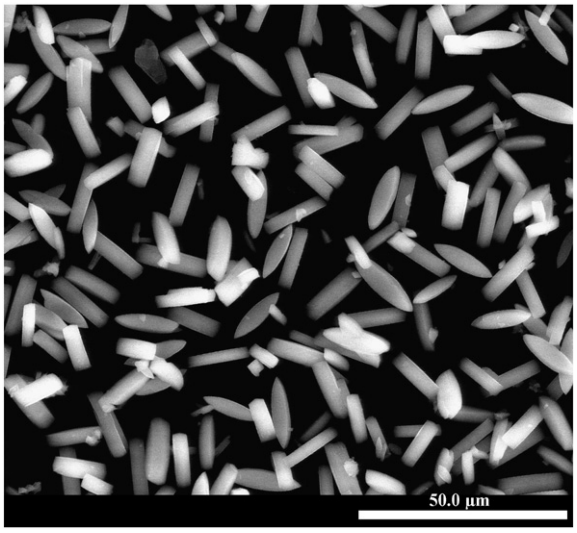

Fig. 4. SEM image of as-synthesized DRM-1.

other phosphates. The structure has subsequently been confirmed by the Rietveld refinement of the PXRD data.

The structure of DRM-1 is constructed from $[Ni_3(P_2O_7)_2(H_2O)_2]^{2-}$ layers stacking in AAA fashion with ammonium cations residing within the interlayer space as shown in Fig. 1, which is similar to those observed in the $K_2[Co_3(P_2O_7)_2(H_2O)_2]$ [30] and $(NH_4)_2[Mn_3(P_2O_7)_2(H_2O)_2]$ [31]. The asymmetric unit contains two crystallographically distinct nickel atoms and two independent phosphorous atoms (Fig. 2). Both nickel atoms are coordinated to six oxygen atoms. The [Ni(1)O_6]-octahedra share trans-edges with two [Ni(2)O_6]-octahedra, while the [Ni(2)O_6]-octahedra share cis-edges with adjacent [Ni(1)O_6]- and [Ni(2)O_6]-octahedron forming a "zigzag" chain of [NiO_6]-octahedra running parallel to the *b* axis. Two phosphorous atoms are tetrahedrally coordinated linked through atom O(5) to form a [P_2O_7] group. The [NiO_6]-based chains are interconnected via [P_2O_7] groups to form layers in the *ab* plane (Fig. 3). The diphosphate group acts as a doubly bidentate ligand bonding to Ni(1) in one [NiO_6]-based chain (via O(1) and O(4)) and Ni(2) in the adjacent chain (via O(3) and O(8)), thus producing a rather distorted geometry ((∠(P(1)–O(5)–P(2) = 127(1)°; d(P–O) = 1.518(14) ~ 1.654(18) Å). Three of the oxygen atoms, O(1), O(3) and O(4), bond to additional nickel atoms and hence are 3-coordinate whilst O(8) and O(2) are 2-coordinate, the latter forming a P(1)–O(2)–Ni(1) bridge. The remaining oxygen of the [P_2O_7] unit, O(6), is coordinated solely to P(2) and points into the interlayer space. The oxygen atom O(7) in the coordination sphere of Ni(2) also points between the layers and does not participate in the linkage between [NiO_6]- and [P_2O_7] units, which should be assigned as a coordinated water molecule O(7)H_2 [31]. A strong net of hydrogen-bonded-of ammonium-layer and interlayer exists in this open-framework. Nitrogen atoms are hydrogen-bonded to the terminal oxygen atoms in adjacent layers (N(1)···O(6), 2.862(18) Å and N(1)···O(6), 2.791(18) Å) and one of the bridging oxygen atom (N(1)···O(8), 2.815(18) Å). The O(7)H_2 group also strongly interacts via hydrogen bonds with the terminal oxygen atom (O(7)···O(6), 2.885(18) Å) and a bridging oxygen in the same layer (O(7)···O(2), 2.670(18) Å).

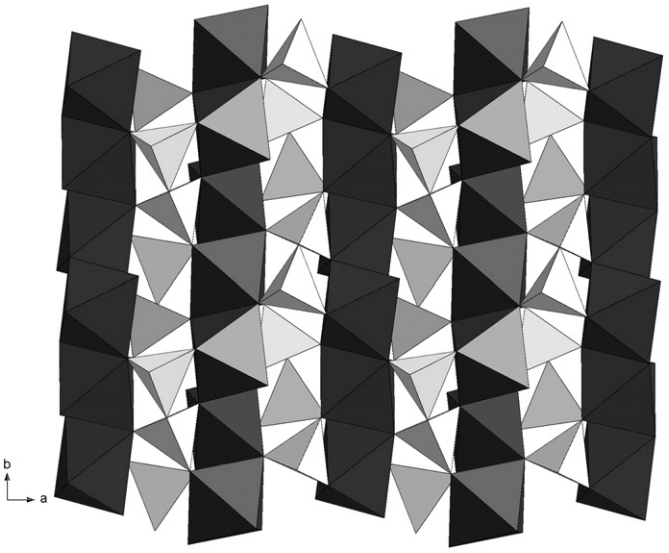

Fig. 3. Polyhedral view of single $[Ni_3(P_2O_7)_2(H_2O)_2]^2$-layer along the c axis. ([NiO_6]-octahedra, dark-grey; [PO_4]-tetrahedra, light-grey).

Thermogravimetric analysis shows up to 800 °C a total weight loss of ca. 15.3% (calculated 14.7%), which corresponds to the removal of the ammonia and water molecules in the framework. The extra weight loss should be caused by a small degree of volatilization of P_2O_5 [30]. The XRD analysis results reveal that the structure collapsed after removal of the occluded ammonium cations and finally transformed to the dense phase $Ni(PO_3)_2$ (PDF-280708).

In conclusion, DRM-1, a new layered nickel diphosphate of chemical composition $(NH_4)_2[Ni_3(P_2O_7)_2(H_2O)_2]$, has been ionothermally synthesized in ionic liquid 1-butyl-3-methyl imidazolium bromide. Its structure has been confirmed by the Rietveld refinement of the PXRD data. Similar to those found in $K_2[Co_3(P_2O_7)_2(H_2O)_2]$ and $(NH_4)_2[Mn_3(P_2O_7)_2(H_2O)_2]$, it consists of layers of $[Ni_3(P_2O_7)_2(H_2O)_2]^{2-}$ with ammonium ions between the layers. Our results provide further evidence for the potential of the ionothermal synthesis in the exploration of new open-framework materials.

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Appendix A. Supplementary material

Further details of the crystal structure may also be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen,