Hydrothermal synthesis and structures of the novel niobium phosphates Ba$_2$[NbOF(PO$_4$)$_3$] and Ba$_3$[Nb$_3$O$_3$F(PO$_4$)$_4$(HPO$_4$)](H$_2$O)$_7$

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The new niobium phosphates Ba$_2$[NbOF(PO$_4$)$_3$] (1) and Ba$_3$[Nb$_3$O$_3$F(PO$_4$)$_4$(HPO$_4$)](H$_2$O)$_7$ (2) have been synthesized in single crystal form by hydrothermal reactions at mild temperatures. Their crystal structures determined from X-ray diffraction data are based on defected derivatives of the NbO(H$_2$O)PO$_4$ layers found in hydrated niobium phosphate. The niobium phosphate layers in 1 or 2 can be derived by removing one half or one quarter of the NbO$_6$ octahedra from the NbO(H$_2$O)PO$_4$ layer, respectively. In compound 1 the layers are separated and are held together by interlayer Ba-O and Ba-F bonds while in 2 the layers are linked by interlayer PO$_4$ tetrahedra to form a framework structure.

Introduction

Crystalline niobium phosphates are of interest because they have potential applications in diverse areas such as luminescence, nonlinear optical materials, ion-exchange and heterogeneous catalysis. In contrast to the large number of vanadium phosphates which are structurally based on the VOPO$_4$ layers of VOPO$_4$$\cdot$2H$_2$O, only a few corresponding niobium phosphates have been reported. Hydrated niobium phosphate, NbOPO$_4$$\cdot$2H$_2$O, consists of layers of composition NbO$_6$(H$_2$O)PO$_4$ in which NbO$_6$ distorted octahedra are connected in their equatorial planes by PO$_4$ tetrahedra via sharing corners. Various types of amines and alcohols can be intercalated between the formally electroneutral NbO$_6$(H$_2$O)PO$_4$ layers. The intercalation chemistry is similar to that first observed in VOPO$_4$$\cdot$2H$_2$O. In Nb$_2$(OH)$_2$(HPO$_4$) (PO$_4$)$_2$$\cdot$2H$_2$O and ANb$_2$(OH)$_2$(PO$_4$)$_3$$\cdot$H$_2$O, A = Na, K, the niobyl phosphate layers are believed to be connected by interlayer PO$_4$ tetrahedra to form 3-dimensional frameworks. The extra-framework monovalent cations are known to be exchangeable with other alkali-, alkaline-earth-metal and alkylammonium ions. However, no accurate structure data are available for these niobium phosphate phases. Similar structures are known and well characterized for vanadium phosphates.

In our hydrothermal synthesis studies, a number of known and new niobium phosphates have been obtained in single crystal form, including [(NbOPO$_4$$\cdot$H$_2$NCH$_2$COOH)$_2$]-[H$_2$PO$_4$][OH, F] that contains glycinium cations bridging the NbOPO$_4$ layers. The crystal structures of most of these new compounds were determined from single crystal X-ray data. Some of them are promising new materials for ion-exchange and intercalation reactions. Here we report the synthesis and structures of two novel barium niobium phosphates Ba$_2$[NbOF(PO$_4$)$_3$] (1) and Ba$_3$[Nb$_3$O$_3$F(PO$_4$)$_4$(HPO$_4$)](H$_2$O)$_7$ (2). The structures of 1 and 2 are based on defect NbO$_6$(H$_2$O)PO$_4$ layers.

Experimental

Synthesis

For the synthesis of compound 1, a solution prepared by mixing 0.17 ml 85% phosphoric acid (EM Science), 33 mg NH$_4$HF$_2$ (99.99%, Aldrich) and 2 ml H$_2$O was sealed together with 231 mg Ba(OH)$_2$$\cdot$8H$_2$O (98%, Aldrich), 14 mg Nd$_2$O$_3$ (99.99%, Aldrich) and 15 mg niobium metal (99.8%, Aldrich) in a flexible Teflon bag in air. The bag was then placed in a RENEX41 reaction vessel of a Leco HR-1B-2 high pressure/high temperature system, and heated at 260 °C under an applied pressure of 120 MPa for 22 h. Colorless plates of 1 formed on the surface of unreacted niobium metal. The yield is about 20% based on Nb. No detectable Nd was found in the crystals of 1 by electron microprobe analysis. Nd$_2$O$_3$ was used in the synthesis aiming at a new compound containing neodymium. Its role in the formation of 1 is not clear.

Compound 2 was synthesized by using a 23 ml Teflon lined autoclave. The starting reagent that contains 0.17 ml 85% phosphoric acid, 33 mg NH$_4$HF$_2$, 2 ml H$_2$O, 231 mg Ba(OH)$_2$$\cdot$8H$_2$O and 15 mg niobium metal, was heated first at 160 °C for 2 days and then at 200 °C for 3 days. Colorless prisms of 2 formed on the surface of unreacted niobium metal together with plates of the impurity phase BaHPO$_4$. The yield is about 10% based on Nb. Efforts to improve the yield and eliminate the impurities by changing the starting composition and temperature were unsuccessful.

Characterization

Chemical compositions were analyzed using a JEOL 8600 electron microprobe operating at 15 keV with a 10 μm beam diameter and a beam current of 30 nA. The measured atomic ratios Ba : Nb : F : F = 2.0 : 1.0 : 2.0 : 0.7 for 1 and Ba : Nb : F = 3.0 : 2.8 : 4.9 : 1.0 for 2 are consistent with the title formulae derived from the structure refinements.

Thermogravimetric analysis for 2 was carried out on a DuPont 2100 TGA system with a heating rate of 5 °C min$^{-1}$ in air after initially equilibrating the sample at 50 °C for 20 min to remove any surface water. A sharp weight loss of 6.8% corresponding to ~5 H$_2$O per formula unit was observed between 100–260 °C. A subsequent gradual weight loss of a further 2.8% began at ca. 260 °C and was completed at ca. 600 °C. The total weight loss of 9.6% observed below 600 °C corresponds to ~7.3 H$_2$O per formula unit.

Single crystal X-ray data were measured on a SMART platform diffractometer equipped with a 1 K CCD area detector using graphite-monochromatized MoK$\alpha$ radiation at
Structure description and discussion

The structure of Ba$_2$(NbOF)(PO$_4$)$_2$ (1)

Fig. 1 shows the coordination environments of the cations in 1. The five oxygen and one fluorine atoms bonding to the niobium atom form a quite regular octahedron, but the Nb atom is displaced from the center to one oxygen corner (O2) leading to a short niobyl Nb–O bond (1.77 Å) and a long Nb–F bond (2.09 Å) in $trans$ positions. The other four equatorial Nb–O bond lengths are between 1.98 and 2.05 Å. The NbO$_5$F octahedron is found randomly disordered over two orientations with opposite apical Nb–O bonds. Each NbO$_5$F octahedron is connected with four PO$_4$ tetrahedra by sharing common corners, with Nb–O–P bond angles ranging from 133.5–146.2°. Neighboring octahedra are bridged by a PO$_4$ tetrahedron in the equatorial plane to form an infinite layer with composition (NbOF)(PO$_4$)$_2$. The layers are stacked along the $a$ axis and are held together by interlayer Ba–O and Ba–F bonds (Fig. 2). The interlayer barium cation has a coordination number of 9 with Ba–(O,F) bond lengths of 2.64–3.09 Å.

Refinements of low symmetry structure models with ordered NbO$_5$F octahedra were unsuccessful.

The structure of Ba$_3$(NbOF)(PO$_4$)$_4$(HPO$_4$)(H$_2$O)$_7$ (2)

In the structure of 2, niobium phosphate layers are linked into a framework structure by interlayer phosphate tetrahedra. Fig. 3 shows the coordination environments of the framework cations. The Nb(1) atom is coordinated to five oxygen atoms and a fluorine atom in an octahedral configuration. Noticeable elongation of the thermal ellipsoids of the Nb(1) and other atom positions (F, O3 in particular) indicates possible orientational disorder of the Nb(1)O$_5$F octahedra similar to that found in compound 1. However, refinements of the models incorporating such disorder were unsuccessful. The Nb(2) atom has an octahedral coordination with a Nb–O bond of 1.72 Å and a long Nb–O bond of 2.18 Å along the apical axis. The four equatorial Nb–O bonds are 2.01–2.02 Å, slightly longer than those of Nb(1) (1.97 Å).

Neighboring Nb(2)O$_6$ octahedra are bridged by two P(1)O$_4$ bonds (Fig. 3).
tetrahedra in the equatorial plane to form an infinite chain of composition NbO$_2$(PO$_4$)$_2$ running along [100]. The chains are cross-linked by the Nb(1)O$_5$F octahedra to form a (010) layer of composition Nb$_3$O$_5$F(PO$_4$)$_4$ (Fig. 4). Each P(1)O$_4$ tetrahedron is connected with two Nb(2)O$_6$ octahedra and one Nb(1)O$_5$F octahedron by sharing corners, with Nb–O–P bond angles in the range 134.4–151.7°. The fourth corner of the P(1)O$_4$ tetrahedron is terminal. The layers are stacked along the [010] direction. Neighboring layers are related by a mirror plane and are cross-linked by the P(2)O$_4$ tetrahedra that share corners with two Nb(2)O$_6$ octahedra from neighboring layers. The interlayer P(2)O$_4$ tetrahedra are disordered among five different orientations (Fig. 3, 5). The barium cations and water molecules are located between the layers. Both are highly disordered with small fractional occupancies. Ba(1–4) have well-defined coordination spheres consisting of framework and water oxygen atoms. An incomplete coordination environment is found for Ba(5) probably because some disordered water molecules could not be located. Ba(5) has the lowest site occupancy and cannot be unambiguously distinguished from disordered water oxygen atoms.

**Relations to other known structures**

In the NbO(H$_2$O)PO$_4$ layer of the hydrated niobium phosphate NbPO$_4$.nH$_2$O each PO$_4$ tetrahedron is connected with four NbO$_6$ octahedra and each NbO$_6$ octahedron is connected with four PO$_4$ tetrahedra in its equatorial plane via sharing corners. If one half of the octahedra are removed from the NbO(H$_2$O)PO$_4$ layer so that two corners of the bridging PO$_4$ tetrahedra are terminal, the resulting layer will be structurally the same as the NbOF(PO$_4$)$_2$ layer of 1. If one quarter of the octahedra are removed from the NbO(H$_2$O)PO$_4$ layer so that one corner of the bridging PO$_4$ tetrahedra is terminal, the resulting layer will be structurally the same as the Nb$_3$O$_5$F(PO$_4$)$_4$ layer of 2.

Topologically the NbOF(PO$_4$)$_2$ layer of 1 is equivalent to the layer of VO(H$_3$PO$_4$)$_2$ and the Fe(H$_2$O)$_2$(SO$_4$)$_2$ layer of the mineral rhomboclase (H$_2$O)$_2$Fe(H$_3$O)$_2$(SO$_4$)$_2$ where the Fe$^{3+}$O$_6$ octahedron has two terminal water oxygen corners. In VO(H$_3$PO$_4$)$_2$ the layers are cross-linked by O–V–O–V–O bonds. The mineral olmsteadite KFe$_2$[NbO$_4$(PO$_4$)$_2$][H$_2$O]$_2$ contains NbO$_4$(PO$_4$)$_2$ layers again closely related to that of 1. The major difference between the two layers is that the two terminal corners of the niobium octahedra are in cis positions in olmsteadite instead of in trans positions as in 1.

The synthetic compound (H$_2$NC$_6$H$_5$NH$_2$)$_2$(VO)$_2$(HPO$_4$)$_2$–(PO$_4$)$_2$[H$_2$O]$_2$ (3) has a layered structure with vanadium phosphate layers similar to the niobium phosphate layer of 2. The vanadium phosphate layers of 3 can also be derived...
by removing one quarter of the octahedra from the NbO(H2O)PO4 layer in a similar way as for the layers of 2. In the layers of 3, however, one third of the remaining octahedra are replaced by VO3 tetragonal pyramids and each of the remaining VO6 octahedra shares an edge with a PO4 tetrahedron, thus only a half of the PO4 tetrahedra have a terminal oxygen corner. The lower valence of V4+ compared to Nb5+ may be a necessary factor for the occurrence of edge-sharing between the PO4 tetrahedra and the VO6 octahedra. This edge-sharing linkage effectively prevents interlayer connection by further phosphate groups in 3 because, except for terminal oxygen of V=O bonds, all the oxygen atoms in the layer are bonded to a V4+ and a P5+ cation. A large family of framework structures formed from MOXO4 layers that are bridged by XO4 tetrahedra are well known9–11 Compound 2 represents an example of forming open framework structures by bridging defect MOXO4 layers.

Conclusions

Hydrothermal reactions at mild temperatures resulted in the new niobium phosphates 1 and 2 in single crystal form. Both compounds contain defected NbO(H2O)PO4 layers. If in an ideal case the fluorine atoms in compound 1 are all located on one side of the layer in an ordered fashion, a strongly polar layered structure will be obtained which may have interesting optical and chemical properties. Intercalation of proper interlayer species such as alkylammonium cations during synthesis may help the ordering, e.g., through hydrogen bonding. Compound 2 is closely related to the known compounds ANb3(OH)2(PO4)3·nH2O, A = Na, K, that are based on non-defected NbO(H2O)PO4 layers. As the latter exhibit well defined ion-exchange properties, similar properties are expected for compound 2.

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Fig. 5 Views of the structure of 2 along c (top) and a axis (bottom). Only one orientation of the interlayer P2O7 tetrahedra is plotted and marked by hatching. Open and solid circles represent water oxygen and barium atom positions respectively.