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Hydrothermal synthesis and structures of $Ba_3(NbO)_2(PO_4)_4$ and $Co_3(NbO)_2(PO_4)_4(H_2O)_{10}$

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The new niobium phosphates $Ba_3(NbO)_2(PO_4)_4$ (**1**) and $Co_3(NbO)_2(PO_4)_4(H_2O)_{10}$ (**2**) have been synthesized in single crystal form by hydrothermal reactions at 250 °C and 170 °C respectively. The crystal structures have been determined from X-ray diffraction data. Both compounds contain NbP_2O_9 complex chains as a fundamental structural unit. The chains are similar to those of the known compound $K_3NbP_2O_9$ and structurally may be considered similar to a slice of the $Zr(HPO_4)_2$ layer in α-zirconium phosphate. In compound **1** the chains are separated and are held together by Ba–O bonds while in **2** the chains are linked by CoO_6 octahedra to form a framework structure.

Introduction

Niobium phosphates are usually prepared by solid state reactions or by reactions in fluxes.[1–8] Hydrothermal syntheses of niobium phosphates are rare but some niobium phosphates have been previously synthesized hydrothermally at rather high temperatures ($\geqslant$600 °C).[9,10] On the other hand, low temperature (<260 °C) hydrothermal reactions are known to be effective in synthesizing phosphates of other metals.[11–15] In particular, Ferey and co-workers reported a series of fluorometallophosphates with open-framework structures synthesized in the systems M–P–F–amine–H_2O with M = Al, Ga, Fe, V and Ti.[16–23] Recently we found that a similar low temperature hydrothermal route is effective in the syntheses of niobium phosphates. Several new niobium phosphates have been synthesized in single crystal form from hydrothermal reactions by using niobium metal and HF_2^- as a mineralizer.[24,25] The low temperature route allows the use of organic structure-directing templates and enhances the possibilities for synthesizing new open-framework niobium phosphates which are expected to be chemically and thermally more stable. For accurate structural and physical characterizations single crystal form products are desired. The studies are of interest because niobium phosphates have potential applications in diverse areas such as luminescence,[26,27] nonlinear optical materials[10] and heterogeneous catalysis.[28]

Here we report syntheses of the novel niobium phosphates $Ba_3(NbO)_2(PO_4)_4$ (**1**) and $Co_3(NbO)_2(PO_4)_4(H_2O)_{10}$ (**2**) and their crystal structures determined from single crystal X-ray diffraction data.

Experimental

Synthesis

In a typical synthesis of compound **1**, a solution was prepared by mixing 0.15 ml 85% phosphoric acid, 33 mg NH_4HF_2 and 116 mg $Ba(OH)_2 \cdot 8H_2O$ in 2 ml H_2O. The solution (pH = 2.9) was then sealed together with 15 mg niobium metal in a flexible Teflon bag in air. The bag was subsequently sealed in a steel reaction vessel filled with water to about 60% volume, and heated at 250 °C for 17 h. Upon cooling to room temperature in 4 h the product was filtered, washed with water and dried in air. Colorless needles of **1** formed as radial aggregates on the surface of unreacted niobium metal. The yield is about 5% based on Nb. Colorless plates of $BaHPO_4$ were recovered as impurities. Efforts to improve the yield and to eliminate the impurity by changing the starting solution composition and temperature were unsuccessful.

Compound **2** was similarly synthesized. A solution prepared by mixing 0.17 ml 85% phosphoric acid, 43 mg NH_4HF_2 and 51 mg 2-aminopyridine in 2 ml H_2O (pH = 2.2) was sealed together with 30 mg niobium and 45 mg cobalt metal, and subsequently heated first at 160 °C for one day then at 170 °C for three days. Pale pink needles of **2** formed as a major phase. The yield is >90% based on niobium. Extensive efforts to eliminate minor impurities (<1%) of tiny colorless plates of an unidentified phase by tuning the synthesis conditions were unsuccessful. Compound **2** was also obtained in the presence of other amines such as methylamine.

Characterization

The 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 : P = 3.0 : 1.9 : 4.1 for **1** and Co : Nb : P = 2.9 : 2.0 : 4.1 for **2** are consistent with the title formulae derived from the structure refinements. For compound **2**, a small amount of fluorine corresponding to 0.3(1) F per formula unit was detected by electron microprobe analysis (see below). Fluoroapatite was used as the analytical standard.

The infrared spectra of **2** were collected with a Galaxy FTIR 5000 series spectrometer using the KBr pellet method. The observed absorption bands at 3484(s), 3216(m), 1634(m) cm^{-1} are typical for water molecules. Other bands were observed at 1128(s), 1059(s), 1019(s), 945(s), 914(s), 605(m), 569(w), 444(w) cm^{-1}. The spectra indicate that the amines used in the syntheses are not incorporated into the structure, which is confirmed by subsequent 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 gradual weight loss of 0.9% corresponding to $0.5H_2O$ per formula unit was observed between 50–130 °C before a sharp weight loss that began at *ca.* 130 °C and was completed at *ca.* 400 °C. A total weight loss of 18.0% was observed below 680 °C, in reasonable agreement

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Table 1 Crystal data and structure refinement for $Ba_3(NbO)_2(PO_4)_4$ (**1**) and $Co_3(NbO)_2(PO_4)_4(H_2O)_{10}$ (**2**)

	1	**2**
Formula	$Ba_3Nb_2O_{18}P_4$	$H_{20}Co_3Nb_2O_{28}P_4$
F. W.	1009.7	954.5
Temperature/K	293(2)	293(2)
Space group	$P\bar{1}$	$P2_1/n$
Unit cell dimensions/Å, °	$a = 4.8898(5)$ $b = 9.076(1)$ $c = 9.521(1)$ $\alpha = 88.815(2)$ $\beta = 78.638(2)$ $\gamma = 78.491(2)$	$a = 5.1259(3)$ $b = 11.1573(8)$ $c = 19.167(1)$ $\beta = 90.171(1)$
Volume/Å^3, Z	405.84(7), 1	1096.2(1), 2
Absorption coefficient/mm^{-1}	9.027	3.660
Reflections collected	2530	6866
Independent reflections	1762 [R(int) = 0.0319]	2480 [R(int) = 0.0779]
R indices [$I > 2\sigma(I)$]^a	$R1 = 0.0550$, $wR2 = 0.1330$	$R1 = 0.0488$, $wR2 = 0.1096$
R indices (all data)	$R1 = 0.0738$, $wR2 = 0.1428$	$R1 = 0.0687$, $wR2 = 0.1174$

$^a R1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. $wR2 = [\Sigma(w(F_o{}^2 - F_c{}^2)^2)/\Sigma(wF_o{}^2)^2]^{1/2}$.

with the theoretical value of 18.9% calculated by assuming that the final product is $Co_3(NbO)_2(PO_4)_4$. The slightly low observed value may be due to partial dehydration during the initial equilibrating stage at 50 °C.

Single crystal X-ray data were measured on a SMART platform diffractometer equipped with a 1K CCD area detector using graphite-monochromatized MoK_α radiation at 293 K. A number of crystals of compound **2** were examined and found all to be twinned. A pseudo-merohedral twin with twin axis [001] was used for data collection and subsequent structure determination. The data were integrated using the Siemens SAINT program.[29] Absorption correction was made using the program SADABS.[30] The structures were solved by direct methods and refined using SHELXTL.[31] For compound **2**, the hydrogen atoms were not located because of the twin. The volume percentage of the two twin components was refined to 46.7(2)% and 53.3(2)%. The small amount of fluorine found in **2** by the microprobe analysis could not be incorporated in the structure refinements and is assumed to be due to substitutions at the water oxygen positions. Crystallographic and refinement details are summarized in Table 1. Atom positions are given in Table 2 and Table 3. CCDC 1145/243. See http://www.rsc.org/suppdata/jm/b0/b003845h/ for crystallographic files in .cif format.

Structure description and discussion

The structure of $Ba_3(NbO)_2(PO_4)_4$ (1)

Table 4 and Fig. 1 show the coordination environments of the cations in **1**. As in many other niobium compounds, the NbO_6 octahedron in **1** is quite regular but the Nb atom is displaced from the center to one corner leading to a short niobyl Nb=O bond (1.73 Å) and a long Nb–O bond (2.22 Å) in *trans* positions. The other four equatorial Nb–O bond lengths are between 1.95 and 2.02 Å. Each NbO_6 octahedron is connected with five PO_4 tetrahedra by sharing common corners, with the niobyl bond being terminal. Neighboring NbO_6 octahedra are bridged by two PO_4 tetrahedra in the equatorial plane to form a $NbO_2(PO_4)_2$ infinite chain. Two such chains are fused together to form a NbP_2O_9 complex chain parallel to [100]. The NbP_2O_9 complex chains having an inversion center symmetry are arranged in the same orientation with the Ba^{2+} cations located between the chains (Fig. 2). The two non-equivalent barium cations both have a coordination number of 10 with Ba–O bond lengths of 2.75–3.28 Å.

Table 2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $Ba_3(NbO)_2(PO_4)_4$ (**1**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U(eq)
Ba(1)	5000	5000	5000	15(1)
Ba(2)	516(2)	7166(1)	886(1)	15(1)
Nb	2565(2)	8922(1)	7283(1)	8(1)
P(1)	3078(6)	8658(3)	3600(3)	9(1)
P(2)	1927(6)	3653(3)	2169(3)	9(1)
O(1)	114(18)	4923(10)	3140(10)	20(2)
O(2)	2637(18)	9392(11)	9030(9)	19(2)
O(3)	2405(17)	8096(9)	5128(8)	11(2)
O(4)	5580(16)	9942(9)	6370(9)	11(2)
O(5)	4589(18)	3046(10)	2846(10)	17(2)
O(6)	262(17)	9225(9)	3035(9)	13(2)
O(7)	2833(19)	4109(10)	634(9)	19(2)
O(8)	383(17)	2338(10)	2107(9)	15(2)
O(9)	4912(18)	7439(10)	2601(10)	18(2)

The structure of $Co_3(NbO)_2(PO_4)_4(H_2O)_{10}$ (2)

Table 5 and Fig. 3 show the coordination environments of the cations in **2**. The NbO_6 octahedra and PO_4 tetrahedra form NbP_2O_9 complex chains that are the same as those of **1** (Fig. 4). The complex chains are laterally linked to form layers parallel to the (001) plane by the $Co(1)O_6$ octahedra. Each $Co(1)O_6$ octahedron shares two axial corners with the NbO_6 octahedra and two equatorial corners with the PO_4 tetrahedra. The other two equatorial corners are occupied by water molecules. The layers are cross-linked into the framework structure by the $Co(2)O_6$ octahedra that share two axial corners with the PO_4 tetrahedra and have four equatorial water molecules (Fig. 4).

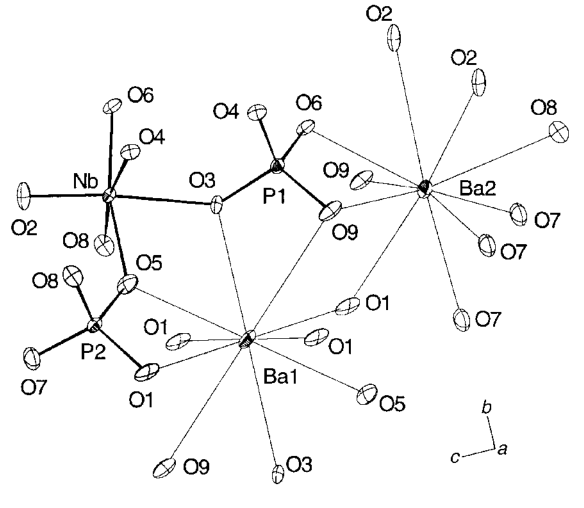

Fig. 1 Local coordination of cations in $Ba_3(NbO)_2(PO_4)_4$. Thermal ellipsoids are at 50% probability.

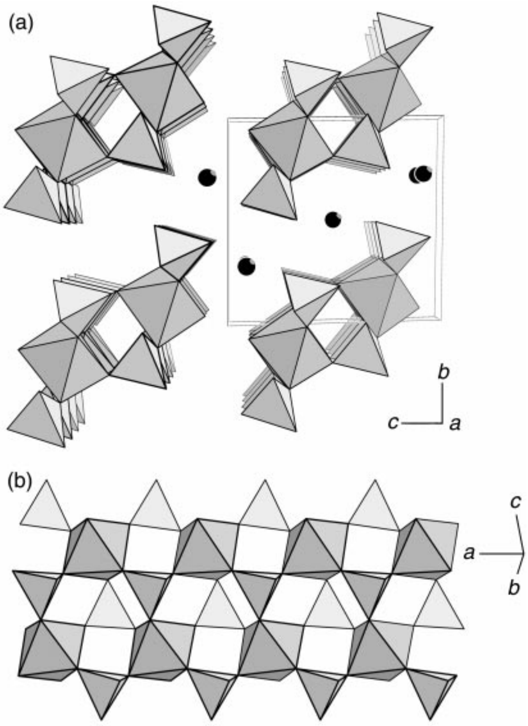

Fig. 2 (a) A view along [100] of the structure of $Ba_3(NbO)_2(PO_4)_4$. Black solid circles represent Ba atoms. (b) The NbP_2O_9 complex chain.

A small amount of fluorine (0.9 atom%) corresponding to 0.3(1) F per formula unit was detected in the sample by electron microprobe analysis. We assume that a small number of H_2O molecules are replaced by F^- ions and that simultaneously protons are introduced at bridging oxygen sites for charge balance. No direct evidence for this assumption can be obtained from the X-ray data. The microprobe analysis clearly indicates the presence of a small amount of fluorine, but because of the large uncertainty in the analysis fluorine has not been included in the title formula. The title formula represents the ideal composition for compound **2**.

The $[Co(2)O_2(H_2O)_4]$ octahedral layer parallel to (001) plane (Fig. 4) could well serve as a composition plane (interface) of the twin. The $Co(2)O_2(H_2O)_4$ octahedra suffer only slight distortion if the two parts separated by the octahedral layer are rotated by 180° around the c axis and then shifted by $\boldsymbol{a}/2+\boldsymbol{b}/4$ relative to each other. Since the volume ratio of the two components is near 0.5/0.5, the twin reflections mimic a higher symmetry in the orthorhombic system ($R_{int}=0.089$). In fact, a rough but chemically reasonable structure model can be obtained in the space group *Pmnb* with disordered Co positions using the same data set.

Table 3 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Co_3(NbO)_2(PO_4)_4(H_2O)_{10}$ (**2**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	*U*(eq)
Nb	2546(2)	2989(1)	288(1)	12(1)
P(1)	−2432(5)	1823(2)	1199(1)	13(1)
P(2)	−7338(5)	997(2)	4266(1)	12(1)
Co(1)	0	0	0	16(1)
Co(2)	−4787(3)	1563(1)	2773(1)	19(1)
O(1)	1989(12)	1605(5)	−115(3)	18(1)
O(2)	−2139(14)	1616(6)	1979(3)	23(1)
O(3)	−8059(12)	−306(5)	4158(3)	18(2)
O(4)	−9320(12)	1615(6)	4751(3)	20(1)
O(5)	−2219(14)	685(5)	775(3)	21(1)
O(6)	−5130(13)	2422(5)	1066(3)	16(1)
O(7)	−349(13)	2765(5)	974(3)	15(1)
O(8)	−4638(12)	1091(5)	4628(3)	19(1)
O(9)	−7328(15)	1681(5)	3583(3)	24(1)
O(10W)	2920(13)	−548(6)	768(3)	25(2)
O(11W)	−7492(18)	457(5)	2210(3)	29(1)
O(12W)	−2154(16)	2738(7)	3316(3)	31(2)
O(13W)	−2806(17)	−24(6)	3184(4)	34(2)
O(14W)	−7072(17)	3042(6)	2344(3)	28(2)

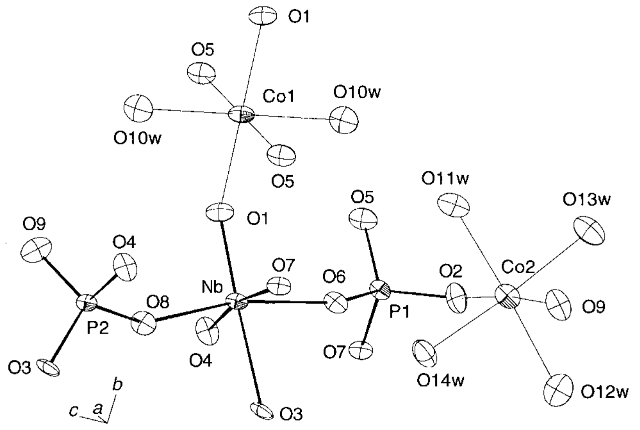

Fig. 3 Local coordination of cations in $Co_3(NbO)_2(PO_4)_4(H_2O)_{10}$. Thermal ellipsoids are at 50% probability.

Relations to other known structures

The NbP_2O_9 complex chains in the structures of **1** and **2** are closely related to the $Zr(HPO_4)_2$ layers in the well-known α-zirconium phosphate $Zr(HPO_4)_2(H_2O)$.[32] The NbP_2O_9 chain can be structurally considered as an infinite [110] slice of the $Zr(HPO_4)_2$ layer in which each ZrO_6 octahedron shares corners with six different phosphate tetrahedra. The terminating niobyl bonds of the NbO_6 octahedra prevent further condensation of the NbP_2O_9 chain into $Nb(PO_4)_2$ layers.

The NbP_2O_9 chains are also found in the known structures of $A_3NbP_2O_9$, A = K, Rb, prepared by solid state reactions.[4,33] Because the number of charge balancing A cations is halved in the structure of $Ba_3(NbO)_2(PO_4)_4$ (**1**), the arrangements of the chains in **1** and in $A_3NbP_2O_9$ are different. The $A_3NbP_2O_9$ structure has a higher symmetry with the monoclinic space group $P2_1/c$. In the more condensed structures of $ANbP_2O_7$, A = K, Rb, NH_4, Tl,[2,8] the same NbP_2O_9 chains are connected into 3-dimensional frameworks by fusing the PO_4 tetrahedra of adjacent chains to form P_2O_7 diphosphate groups. In all the known structures of $A_3NbP_2O_9$ and $ANbP_2O_7$ strong distor-

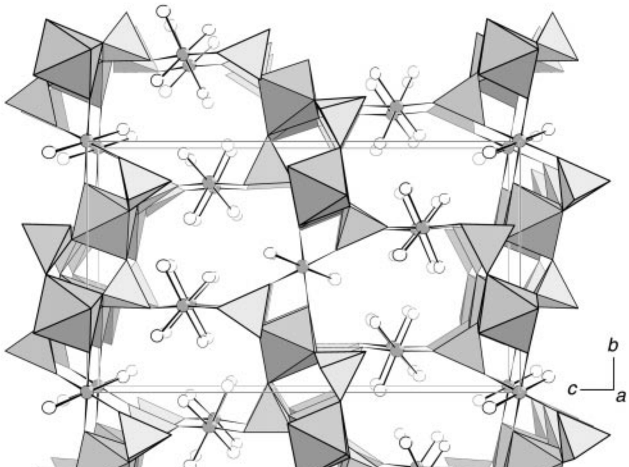

Fig. 4 A view along [100] of the structure of $Co_3(NbO)_2(PO_4)_4(H_2O)_{10}$. Grey and white circles represent Co atoms and water oxygen atoms respectively.

Table 4 Selected bond lengths [Å] and angles [°] for $Ba_3(NbO)_2(PO_4)_4$ (**1**)

Ba1–		Ba2–				
O1	2.754(9) × 2	O6	2.768(8)			
O5	2.801(8) × 2	O7	2.775(9)			
O3	2.837(8) × 2	O7	2.806(9)			
O9	3.15(1) × 2	O9	2.867(9)			
O1	3.254(9) × 2	O2	2.87(1)			
		O1	2.93(1)			
		O8	2.979(9)			
		O9	2.994(9)			
		O2	3.19(1)			
		O7	3.275(9)			
Bond lengths		Bond angles				
Nb–		O2	O4	O8	O6	O5
O2	1.734(9)					
O4	1.948(8)	96.2(4)				
O8	2.005(8)	93.4(4)	169.8(3)			
O6	2.012(8)	95.6(4)	88.0(3)	94.5(3)		
O5	2.023(9)	96.9(4)	90.1(4)	85.2(4)	167.5(3)	
O3	2.220(8)	174.3(4)	88.3(3)	81.9(3)	88.1(3)	79.5(3)
P1–		O9	O3	O4		
O9	1.498(9)					
O3	1.528(9)	111.5(5)				
O4	1.545(8)	113.0(5)	108.5(5)			
O6	1.564(8)	108.2(5)	110.2(5)	105.3(5)		
P2–		O1	O7	O8		
O1	1.511(8)					
O7	1.515(9)	113.9(6)				
O8	1.542(9)	112.1(5)	106.5(5)			
O5	1.563(9)	106.4(5)	110.5(5)	107.3(5)		

Table 5 Selected bond lengths [Å] and angles [°] for $Co_3(NbO)_2(PO_4)_4(H_2O)_{10}$ (**2**)

Bond lengths		Bond angles				
P1–		O5	O2	O6		
O5	1.510(6)					
O2	1.520(6)	113.2(4)				
O6	1.556(7)	109.8(4)	108.1(4)			
O7	1.560(6)	111.6(4)	107.9(4)	105.9(4)		
P2–		O3	O9	O4		
O3	1.515(6)					
O9	1.515(6)	111.5(4)				
O4	1.542(6)	110.5(4)	107.4(4)			
O8	1.550(6)	110.1(3)	110.4(4)	106.8(4)		
Nb–		O1	O4	O8	O7	O6
O1	1.749(6)					
O4	1.961(6)	95.7(3)				
O8	1.975(6)	94.9(3)	90.6(3)			
O7	2.001(6)	93.4(3)	169.5(3)	93.8(3)		
O6	2.009(6)	98.4(3)	88.6(3)	166.8(2)	84.9(3)	
O3	2.194(6)	176.4(3)	87.8(3)	85.8(2)	83.0(2)	81.0(2)
Co1–		O5	O5	O1	O1	O10W
O5	2.024(6)					
O5	2.024(6)	180.00				
O1	2.073(6)	91.7(2)	88.3(2)			
O1	2.073(6)	88.3(2)	91.7(2)	180.00		
O10W	2.183(6)	89.8(2)	90.2(2)	88.7(2)	91.3(3)	
O10W	2.183(6)	90.2(2)	89.8(2)	91.3(2)	88.7(3)	180.00
Co2–		O9	O2	O11W	O12W	O14W
O9	2.035(7)					
O2	2.043(7)	174.4(3)				
O11W	2.145(8)	90.4(3)	94.1(3)			
O12W	2.148(8)	89.6(3)	85.7(3)	177.5(3)		
O14W	2.182(7)	83.9(3)	93.1(3)	84.3(3)	93.2(3)	
O13W	2.187(7)	94.3(3)	89.1(3)	90.8(3)	91.7(3)	174.8(3)

tions of the NbO_6 octahedra similar to that in the two title compounds are observed. In comparison β-$TaH(PO_4)_2$ has a framework structure which is similar to but different from that of $ANbP_2O_7$.[34] The framework is formed by connection of TaP_2O_9 chains which are similar to the NbP_2O_9 chain, through sharing the sixth corner of the TaO_6 octahedra with the PO_4 tetrahedra of adjacent chains, without formation of P_2O_7 dimers. The strong tendency of tantalum to form more regular TaO_6 octahedra makes such connections possible.

Conclusions

Hydrothermal reactions under mild conditions resulted in the new niobium phosphates **1** and **2** in single crystal form. Both compounds contain the NbP_2O_9 complex chain as a fundamental structural unit. The same complex chains are found in the known compounds $A_3NbP_2O_9$ and $ANbP_2O_7$ prepared by solid state reactions. Since the compounds $ANbP_2O_7$ have been found to exhibit a high luminescence efficiency at ambient temperature and below,[27] measurements of similar properties of the title compounds are of interest.

Acknowledgements

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