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Niobate and Tantalate Pyrochlores: Soft Synthesis by the Fluoride Route

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A series of pyrochlores $A(Nb,Ta)_2(O,OH,F)_6(nH_2O)$, (A = NH_4, K, Rb, Cs) have been synthesized by hydrolysis of aqueous solutions of oxofluoroniobic (H_2NbOF_5) and fluorotantalic (H_2TaF_7) acids. This new method allows preparation of nanocrystalline niobate pyrochlores (crystal size 10–20 nm) by simple precipitation with subsequent boiling; tantalate analogues can be obtained by soft hydrothermal treatment. The synthesized compounds include new pyrochlores $NH_4Nb_2O_5(OH,F)$, $NH_4Ta_2O_5(OH,F)\cdot nH_2O$ and $K_{1-x}Nb_2(O,OH)_5F\cdot nH_2O$ as well as the already known $CsNb_2O_5F$, $Rb_{1-x}Nb_2(O,OH)_5F$, $CsTa_2O_5F$ and their hydroxyl analogues. Ion-exchange experiments revealed that $K_{0.7}Nb_2(O,OH)_5F\cdot nH_2O$ exhibits strong selective uptake of Pb^{2+} from aqueous solutions, a feature not previously reported for pyrochlores. The facilitating role of fluoride ions in the synthesis of pyrochlores is discussed in comparison with zeolite synthesis, and the technological applicability of the new method is also presented in the paper.

Introduction

Niobate and tantalate pyrochlores of the general formula $A_{1-2}(Nb,Ta)_2(O,OH,F,H_2O)_{6-7}$ (A = large-radius cation) are well known for proton and ionic conductivity, which render them useful for applications in solid electrolyte fuel cells;[1–3] they are also used as catalysts for the conversion of hydrocarbons.[4] The basic approach for the preparation of these compounds is a high-temperature solid-state synthesis introduced in 1967.[5] Hydrothermal alkaline treatment of Ta_2O_5 was first reported by Kumada et al. as a way to synthesize tantalate pyrochlores.[6] Since that time, modifications of the hydrothermal method have been applied to the preparation of pyrochlore-type $Ca_2Nb_2O_7$, $Ca_2Ta_2O_7$, $K_{0.88}H_{1.12}Nb_2O_6\cdot 1.58H_2O$ and $KLnTa_2O_7$.[7,3,8] Low-temperature aqueous chemistry was not considered as a route to Nb- and Ta-pyrochlores. The observed inability of Nb and Ta to form pyrochlore-type phases in aqueous solutions under ambient conditions is a consequence of the hydrolytic decomposition of niobium and tantalum compounds at very low pH (1–1.5) resulting in the precipitation of amorphous hydroxides.[9–12] Several methods were proposed to avoid low-pH hydrolysis of Nb and Ta salts, all of them implementing complexation into stable anions such as carboxylato or peroxido complexes.[10–14] Among other anionic species of Nb and Ta, one should point at their remarkably stable fluorido complexes, which were thoroughly investigated, as they are the key intermediates in industrial processing of both metals.[15,16] Surprisingly, however, products of alkaline treatment of fluoroniobates and fluorotantalates have not been studied to date. We found that alkaline hydrolysis of oxofluoroniobic (H_2NbOF_5) and fluorotantalic (H_2TaF_7) acids under controlled conditions results in the formation of nanocrystalline pyrochlores, among which are the new compounds $NH_4Nb_2O_5(OH,F)$, $NH_4Ta_2O_5(OH,F)\cdot nH_2O$ and $K_{1-x}Nb_2(O,OH)_5F\cdot nH_2O$. Comparative ion-exchange experiments carried out with $NH_4Nb_2O_5(OH,F)$ and $K_{0.74}Nb_2(O,OH)_5F\cdot nH_2O$ revealed that the latter compound possesses strong selective affinity for Pb^{2+}. Fluoride ion promotion extensively employed in the syntheses of zeolites[17] can be extended into the area of transition-metal framework oxides. The fluoride method is the simplest way to synthesize the pyrochlore compounds reported to date. A distinguishing advantage of this route is its technological applicability: fluoro complexes are the intermediates in the industrial processing of Nb and Ta, so that pyrochlores can be prepared directly from fluoride strip solutions, and the stage of pure oxide preparation can be omitted.

Results and Discussion

Synthesis

Hydrolytic decomposition of aqueous solutions of H_2NbOF_5 under a controlled excess of alkalis (molar ratio Nb/AOH between five and six for A = K, Rb, Cs; molar

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Table 1. Chemical data and Rietveld refinement details for the synthesized pyrochlores.

Simplified formula	Sample[a]	Form.$_A$[b]	Form.$_F$[b]	a (Å)	R_p (%)	R_{wp} (%)	R_B (%)	χ^2
$NH_4Nb_2O_5(OH,F)$	NH3Nb-B	0.97	0.34	10.540(3)	1.5	1.9	0.8	1.01
$NH_4Nb_2O_5(F,OH)$	NH3Nb-HT	1.19	0.72	10.539(2)	2.7	3.4	6.5	4.03
$NH_4Ta_2O_5(OH,F)\cdot nH_2O$	NH3Ta-HT	0.95	0.37					
$K_{0.7}Nb_2(O,OH)_5F\cdot nH_2O$	KNb-B	0.74	0.87					
$KNb_2O_5F\cdot 1.2H_2O$	KNb-HT	0.94	0.97	10.6501(3)	6.9	9.1	5.1	2.18
KTa_2O_5OH	KTa-HT	0.97	0.10	10.602(2)	0.9	1.2	0.6	4.43
$Rb_{0.7}Nb_2(O,OH)_5F$	RbNb-B	0.68	0.99	10.502(5)	4.3	5.5	2.9	1.79
$Rb_{0.8}Nb_2(O,OH)_5F$	RbNb-HT	0.81	0.96	10.492(3)	4.3	5.8	2.0	4.39
$RbTa_2O_5OH$	RbTa-HT	0.93	0.01	10.536(2)	2.2	2.9	1.7	2.63
$CsNb_2O_5F$	CsNb-B	0.95	1.05	10.538(4)	1.6	2.0	1.0	5.42
$CsNb_2O_5F$	CsNb-HT	1.01	1.02	10.540(2)	2.9	3.7	3.0	2.79
$CsTa_2O_5F$	CsTa-HT	1.03	0.94	10.48(1)	1.2	1.5	0.6	2.92

[a] Last letters indicate conditions of synthesis: B = boiling, HT = hydrothermal. [b] Formula amounts of the corresponding alkali cation (A) and fluorine (F) calculated on the basis of two atoms of (Nb,Ta) per formula unit.

ratio Nb/NH_3 ca. 20) with subsequent short-time boiling always results in the formation of pyrochlore-type compounds (Table 1). Synthesized pyrochlores appear as fine white powders and are easily identified with conventional XRD (Figure 1). TEM observations reveal that crystallites of such synthesized "boiled" pyrochlores form botryoidal or spherulitic aggregates, with a typical crystallite size of 10–20 nm [10–20 edges of the pyrochlore unit cell (Figure 2a)]. Hydrothermal treatment of the same kinds of reaction mixtures improves the crystallinity of niobate pyrochlores, producing crystal sizes up to 50–60 nm with perfect octahedral crystal shape (Figure 2b). Formation of pyrochlores with solutions of H_2TaF_7 is more difficult. Simple boiling of precipitated tantalum hydroxide in the parent alkaline solutions gives amorphous products, which cannot be ascribed to any structure type. Hydrothermal treatment, however, yields pyrochlores as well (Table 1, Figure 1). Tantalate pyrochlores are always poorly crystallized, with uneven crystallite shape and have a crystallite size not exceeding 10–20 nm (Figure 2c). It should be mentioned that the given acid/alkali ratios are essential requirements for the successful synthesis of K-, Rb- and Cs-pyrochlores. Addition of an amount of alkali in excess of the given ratios to the reaction mixture results in quick dissolution of precipitated Nb and Ta hydroxides due to formation of readily soluble hexaniobates and hexatantalates (Lindqvist

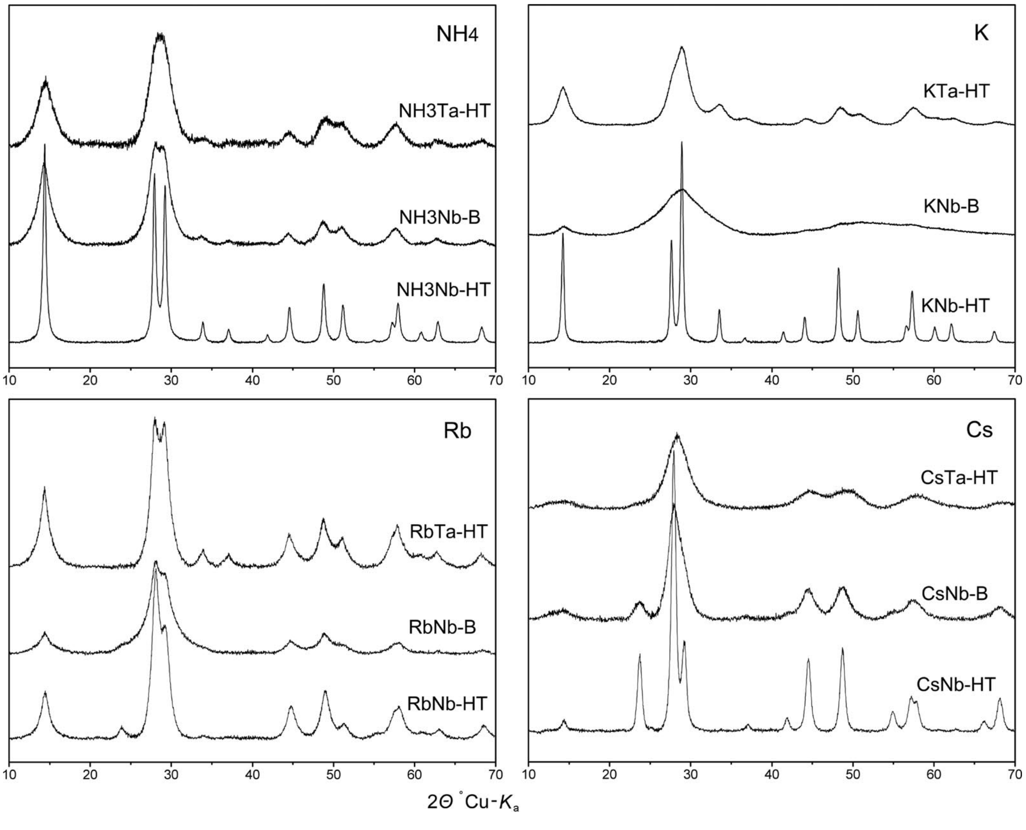

Figure 1. Powder XRD patterns of synthesized pyrochlores. Sample codes according to Table 1.

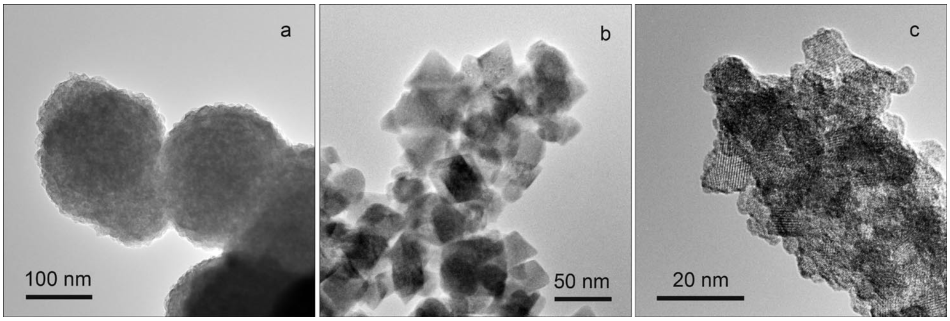

Figure 2. Typical aggregate morphology of synthesized pyrochlores. (a) $RbNb_2O_5(OH,F)$ (prepared by boiling). (b) $NH_4Nb_2O_5(F,OH)$ (hydrothermal). (c) $RbTa_2O_5OH$ (hydrothermal).

salts).[18,19] As a consequence, the fluoride method can be successfully employed for the preparation of Lindqvist compounds, offering an alternative to the recently reported peroxide method,[20] but this feature requires further separate study.

Crystal Structure and Chemical Composition

The results of Rietveld refinements for the ten synthesized pyrochlores are given in Table 1, and their structural parameters are summarized in Table 2. As it has been described elsewhere,[21] ideal pyrochlores crystallize in the cubic system, space group *Fd*-3*m*. As no evidence was found for a possible symmetry reduction, the refinements were carried out in the space group *Fd*-3*m* (origin choice 2). The pyrochlore structure with fully occupied sites corresponds to a general formula $A_2B_2X_6Z$. Here, the B site (16*c*) denotes octahedrally coordinated framework-forming cations, typically multivalent transition metals, while the A site (16*d*, distorted hexagonal bipyramid) is occupied by intrachannel cations of larger radius (or by neutral molecules). X (48*f*) is a framework-forming anion, usually O, F or OH, while Z (site 8*b*) is an intrachannel anion or a neutral molecule. In so-called defect pyrochlores, one of the intrachannel sites becomes vacant. This feature makes cation migration through the framework possible, and defect pyrochlores possess proton and ionic conductivity.[1–3] A special case may occur when a cation vacancy is located on site A. Then charge-balancing cations occupy the "anionic" site Z (8*b*). Defect pyrochlores of this type are also known as β-pyrochlores;[22] their formula can be written as $\square_2B_2X_6Z$ (□ is a vacancy on site A), and the cation ratio B/Z is equal to 2.

The chemical compositions of the synthesized compounds (Table 1) fall into the area of defect pyrochlores. Unfortunately, such results derived from bulk chemical data do not necessarily imply that the corresponding pyrochlores are really "defect", owing to the possibility of partial (1/2) occupancy of site 16*d* in "perfect" structures. Thus, correct treatment of chemical data always requires structural refinement. Another analytical problem, which is common especially for nanostructured materials, is to distinguish between adsorbed and weakly chemically bound H_2O. Due to their high surface area, pyrochlores synthesized by the fluoride method contain variable and significant amounts of adsorbed water. Both adsorbed and weakly chemically bound water evolve at approximately 100 °C and could not be resolved by using conventional TGA techniques.[23] From a crystallographic point of view, insertion of one molecule of intrachannel H_2O per formula unit may result in the formation of the ideal pyrochlore structure instead of a defect one. The results of Rietveld refinements suggest that the majority of pyrochlores synthesized by the fluoride method belong to defect structures.

Table 2. Structural parameters for the synthesized pyrochlores. Sample codes according to Table 1.

Sample	Site 16*c*[a]	Sites 8*b* and 16*d*			Site 32*e*			Site 16*d*	
	B_{iso}	Site	Occupancy[c]	B_{iso}	Occupancy	*x*	B_{iso}	*x*	B_{iso}
NH_4Nb-B	1.18(8)	8*b*	$N_{1.00}$	7.7(7)				0.3180(3)	0.83[b]
NH_4Nb-HT	2.12(3)	8*b*	$N_{1.00}$	11.6(4)	$H_{1.00}$	0.428[d]		0.3134(2)	0.83(7)
KNb-HT	3.23(2)	16*d*	$K_{0.50}$	6.11(9)	$(H_2O)_{0.30}$	0.4170(4)	1.6(3)	0.3126(2)	1.46(6)
KTa-HT	1.65(3)	16*d*	$K_{0.50}$	2.66(1)				0.3111(2)	1.00[b]
RbNb-B	3.5[b]				$Rb_{0.23}$	0.4086(2)	1.2(2)	0.3153(5)	2.4(4)
RbNb-HT	3.5(2)				$Rb_{0.21}$	0.4008(3)	3.5(2)	0.3153(3)	2.5(2)
RbTa-HT	0.61(6)				$Rb_{0.25}$	0.4096(5)	9.3(5)	0.3172(5)	1.3(3)
CsNb-B	2.06(4)	8*b*	$Cs_{1.00}$	5.66(5)				0.3157(2)	1.37(8)
CsNb-HT	2.00(4)	8*b*	$Cs_{1.00}$	2.43(5)				0.3162(4)	1.00[b]
CsTa-HT	1.65(8)	8*b*	$Cs_{1.00}$	5.5(1)				0.3131(5)	2.9(2)

[a] Fractional coordinates of sites: 16*c* (Nb,Ta)(0; 0; 0); 16*d* (1/2; 1/2; 1/2); 8*b* (3/8; 3/8; 3/8); 32*e* (*x*; *x*; *x*); 48*f* (O,OH,F) (*x*; 1/8; 1/8). [b] Displacement parameters could not be directly refined and were fixed at reasonable values. [c] Occupancies of site 8*b* were fixed according to results of chemical analyses and charge-balance calculations. [d] Position of hydrogen in NH_4^+ as located by difference mapping (*SHELX-97*).

The new, hydrothermally synthesized $KNb_2O_5F{\cdot}1.2H_2O$, is the only non-defect pyrochlore in our series. Its crystal structure is closely related to that of $K_{0.88}H_{1.12}Nb_2O_6{\cdot}1.58H_2O$.[3] Molecular water seems to be essential for the stabilization of the pyrochlore structure of this compound, because anhydrous KNb_2O_5F was found to crystallize in the tetragonal tungsten bronze type.[24,25] All the water from $KNb_2O_5F{\cdot}1.2H_2O$ evolves in one step below 180 °C. The chemical composition of K-Nb pyrochlore, obtained by boiling, corresponds to $K_{0.74}Nb_2(O,OH)_5F{\cdot}nH_2O$. Contrary to its hydrothermal counterpart, this "boiled" pyrochlore gives rather poor diffraction patterns, although there is no doubt that it indeed belongs to the pyrochlore type (Figure 1). TEM observations show that the crystallite size of $K_{0.74}Nb_2(O,OH)_5F{\cdot}nH_2O$ varies from 5 to 30 nm. Such broad size distribution results in a specific shape of the reflections in the powder XRD patterns, which cannot be described by the pseudo-Voigt function used in the X-ray Rietveld analysis. As a result, structural refinement could not be performed for this sample.

Potassium tantalate pyrochlore was first synthesized by Kumada et al.,[6] who represented its formula as $K_{1-x}H_xTaO_3{\cdot}nH_2O$. Later Duan et al.[26] repeated this synthesis, carried out structural refinement by the Rietveld method and proposed that this pyrochlore possesses a defect structure with chemical composition corresponding to $KTa_2(O,OH)_6{\cdot}1.8H_2O$. They found that the A sites are half occupied by K^+ ions. As a part of our study, an aqueous $KOH\text{-}H_2TaF_7$ system was employed for the synthesis of K-Ta pyrochlore. The resulting product has crystal sizes in the range 10–20 nm, contrary to the rather well-crystallized (ca. 1 µm) product obtained by Duan et al. In contrast with the latter study, Rietveld refinement did not reveal molecular water in our pyrochlore, yielding the chemical formula KTa_2O_5OH.

$NH_4Nb_2O_5X$ (X = OH, F) are new compounds not reported to date. Ammonium pyrochlore synthesized by boiling is hydroxyl-dominant; the compound prepared under hydrothermal conditions is fluoride-dominant (Table 1). These pyrochlores are of particular technical interest, because precipitation of niobium hydroxide by ammonia from fluoride strip solutions is a key step in the industrial production of Nb_2O_5.[15,16] Consequently, $NH_4Nb_2O_5(OH,F)$ may be considered as the technologically most easily accessible pyrochlore, as its synthesis requires just a slight deviation (i.e., short-time boiling of the reaction mixture) from the main process flow, and the stage of preparation of pure Nb_2O_5 can be omitted. There are two ammonium pyrochlores reported to date, and both are tungsten-bearing NH_4MWO_6 (M = Nb, Ta) obtained by solid-state methods. The structures of NH_4MWO_6 were studied in conjunction with their proton conductivity and pressure-induced volume expansion.[27–29] Examination of our NH_4-Nb pyrochlores revealed that they relate to defect frameworks like NH_4MWO_6, but their structures, unlike NH_4MWO_6, do not show any deviations from space group *Fd*-3*m*. In addition, in the case of hydrothermally synthesized $NH_4Nb_2O_5(F,OH)$, electron difference maps using data from single-crystal methods (SHELX-97) enabled the location of hydrogen in position 32*e*. This hydrogen site appears crystallographically reasonable, as it corresponds to perfect tetrahedral coordination of nitrogen in NH_4^+, with N–H bond lengths of 0.96(2)(esd) Å (Figure 3). The results of Rietveld refinements for both NH_4-Nb pyrochlores are very similar (Table 2), so one can assume that $NH_4Nb_2O_5(OH,F)$, prepared by boiling, also contains tetrahedrally coordinated nitrogen in the ammonium ion.

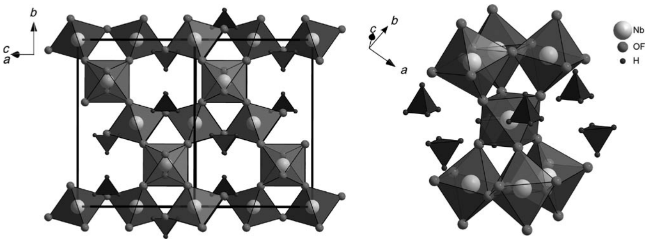

Figure 3. Crystal structure of $NH_4Nb_2O_5(OH,F)$.

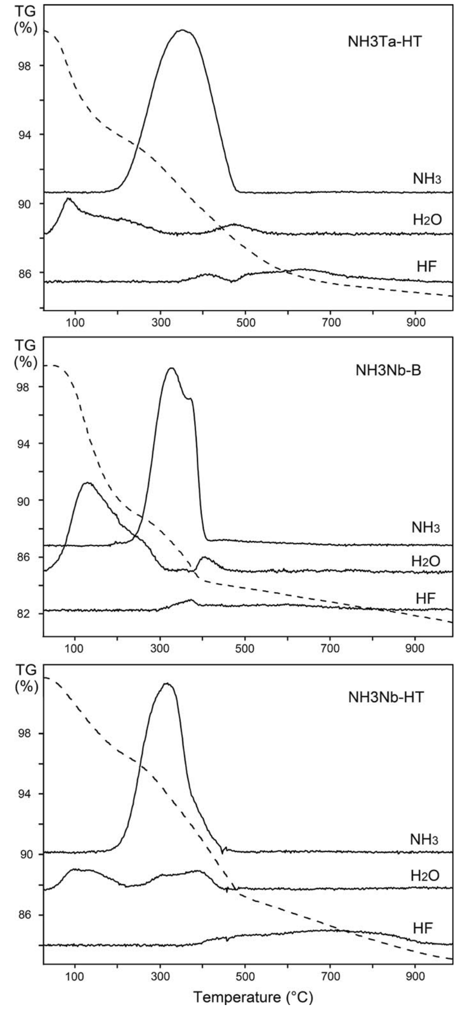

Figure 4. TG and gas evolution curves for ammonium pyrochlores. Sample codes according to Table 1.

Owing to the absence of Rietveld data, the chemical formula of $NH_4Ta_2O_5(OH,F)\cdot nH_2O$ was derived from chemical and TGA-FTIR (Table 1) analyses. The patterns of thermal decomposition of all three NH_4-pyrochlores are similar and can be subdivided into three main steps (Figure 4). The first step, from approximately 30 to 150 °C, corresponds to a loss of weakly bound water. As Rietveld refinements of NH_4-Nb pyrochlores did not reveal any molecular H_2O, this step can be ascribed to the loss of adsorbed water. The nature of the water in $NH_4Ta_2O_5(OH,F)\cdot nH_2O$ remains unresolved. The second step, at 150–350 °C, is connected with the evolution of NH_3 and high-temperature H_2O, while the third step is assumed to be the evolution of structural hydroxyl water. Note that the evolution of NH_3 from NH_4MWO_6, as reported earlier, occurs at much higher temperatures, viz. between 440 and 505 °C.[30] The last component evolved from ammonium pyrochlores is fluorine, which is released as HF in the temperature range from 300 to 900 °C.

A series of synthesized Rb and Cs compounds relates to β-pyrochlores. In the caesium group, Cs^+ fully resides on "anionic" Z ($8b$) sites, while in the rubidium compounds, Rb^+ partially (ca. 1/4) occupies the $32e$ position (x, x, x) (this site can be derived from ideal $8b$ by off-centring). Fluoride pyrochlores of this series, $RbNb_2O_5F$, $CsNb_2O_5F$ and $CsTa_2O_5F$, were formerly prepared by high-temperature calcination;[5] their hydroxyl-substituted analogues, $Rb_{1-x}Nb_2O_5OH$ and $RbTa_2O_5OH$, have not been reported to date. For the tantalate analogue, however, there may be structural similarity with previously reported rubidium oxide tantalate pyrochlore, $2Rb_2O\cdot 5Ta_2O_5$.[31] Structural and chemical data for Cs- and Rb-pyrochlores are summarized in Tables 1 and 2.

Ion Exchange

The pyrochlore framework is tolerant to intrachannel cation substitutions. Ion-exchange properties of antimonate, titanate and tungstate pyrochlores were studied in conjunction with their potential application for treatment of nuclear waste solutions.[32–34] These studies revealed the high selectivity of some antimonate pyrochlores for Sr^{2+} uptake. In the meantime, no data were reported on selective exchange properties of niobate and tantalate pyrochlores. In the present work, we have carried out preliminary cation-exchange experiments with two new pyrochlores, $NH_4Nb_2O_5(OH,F)$ and $K_{0.7}Nb_2(O,OH)_5F\cdot nH_2O$, both prepared by a readily accessible method, (i.e. precipitation with subsequent boiling). Seven cations, all being potential water contaminants, were chosen for examination. The results of exchange experiments are presented in Table 3. An obvious consequence can be deduced from the listing, viz. that both pyrochlores possess high affinity to large divalent cations. This observation is in general compliance with previous studies for selective uptake of radioactive Sr^{2+}. However, the very strong selectivity of $K_{0.7}Nb_2(O,OH)_5F\cdot nH_2O$ toward Pb^{2+} was unexpected and offers a challenge for future studies.

Table 3. Cation concentrations in supernatant solution and distribution coefficients (K_D) for $NH_4Nb_2O_5(OH,F)$ (**1**) and $KNb_2O_5F\cdot nH_2O$ (**2**).

Cation	Concentration (mg/L)			K_D (mL/g)	
	Initial	Residual (for **1**)	Residual (for **2**)	(for **1**)	(for **2**)
Sr^{2+}	48.63	3.41	22.06	2651	241
Ba^{2+}	42.94	0.69	4.83	12336	1578
Cd^{2+}	57.48	54.05	41.13	13	80
Pb^{2+}	53.90	0.70	0.13	15266	82723
Co^{2+}	55.30	52.69	44.90	10	46
Ni^{2+}	55.64	53.00	45.21	10	46
Cu^{2+}	50.47	44.33	23.26	28	234

Discussion

The nature of fluoroniobate and fluorotantalate complexes in acid aqueous media was a subject of intensive investigations to account for their technological applications.[35–38] By studying solubility isotherms and by use of spectroscopic data (Raman and NMR) it was found that solutions of fluoroniobates in aqueous HF, in a concentration range up to 10 M, contain solely $[NbOF_5]^{2-}$ anions at any existing Nb concentration. Further increase in HF concentration leads to the formation and then continuous predominance of $[NbF_6]^-$ ions. The behaviour of Ta-HF-H_2O systems is different. Tantalum does not form oxidofluorido complexes in aqueous solutions; at HF concentrations up to 20 M, it occurs as $[TaF_7]^{2-}$, with further formation of $[TaF_6]^-$ similar to Nb. Thus in diluted (0.33 M for Nb or Ta) solutions used in the present work, two different anion types exist and are subject to subsequent hydrolysis: the distorted octahedron of $[NbOF_5]^{2-}$ and $[TaF_7]^{2-}$ with sevenfold coordinated Ta (Figure 5).[39,40] Here, one can draw some analogy with the fluoride route in silicate syntheses. The facilitating role of the fluoride ion is a feature successfully employed for the preparation of zeolites and sodalites.[17] Injection of F^- in silicate systems under acidic conditions yields hexafluorosilicate ions. It was suggested that subsequent hydrolysis of $[SiF_6]^{2-}$ by addition of alkalis results in the formation of polycondensed hydroxyl-substituted silicate complexes, giving rise to a diversity of synthesized zeolites. In the case of aqueous solutions of $[NbOF_5]^{2-}$ and $[TaF_7]^-$, a similar approach can be proposed. Indirect evidence of such behaviour of Nb and Ta fluorido complexes is that hydroxides of Nb and Ta precipitated by ammonia from industrial fluoride solutions containing 1.5–2 wt.-% of fluorine and 0.2 wt.-% of NH_3 are in fact complex hydrated fluorohydroxides.[41] It is noteworthy that hydrolysis of the octahedral $[NbOF_5]^{2-}$ ion does not result in changes in the coordination of Nb, thus $[NbOF_5]^{2-}$ may be considered as a "ready-to-use" template for building up octahedral pyrochlore frameworks. In the case of fluorotantalates, hydrolysis requires complete rebuilding of the coordination sphere of Ta, from sevenfold coordination in $[TaF_7]^-$ to octahedral coordination in the framework composed of $[Ta(O,OH,F)]_6$. For the fluorometalate-alkali systems described in this paper, these differences in coordination of Nb and Ta in precursor complexes may explain the better crystallization behaviour of niobate pyrochlores compared with their tantalate analogues.

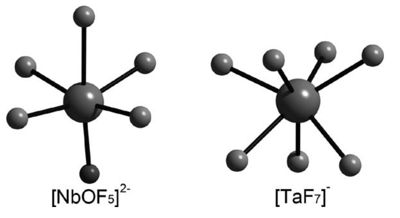

Figure 5. Coordination of Nb and Ta in oxofluoroniobate and fluorotantalate anions (based on data from refs.[39,40]).

Conclusions

Alkaline hydrolysis of oxofluoroniobic and fluorotantalic acids is a new and simple method for the synthesis of niobate and tantalate pyrochlores allowing their preparation under near-ambient or soft hydrothermal conditions. A representative series of new compounds has been synthesized, including $NH_4Nb_2O_5(OH,F)$, $KNb_2O_5F\cdot1.2H_2O$, $RbTa_2O_5OH$ and KTa_2O_5OH. Some previously known pyrochlores, e.g. $CsNb_2O_5F$, which are conventionally synthesized by high-temperature calcination, can be obtained by cold precipitation and boiling. Preliminary ion-exchange experiments reveal the strong affinity of $NH_4Nb_2O_5(OH,F)$ and $KNb_2O_5F\cdot1.2H_2O$ to large-radius divalent cations, in particular to Pb^{2+}. The fluoride method is technologically easily accessible because fluoroniobate and fluorotantalate solutions are intermediates in the industrial processing of Nb and Ta. It is an essential advantage of the fluoride synthesis that nanocrystalline pyrochlores can be produced directly from industrial fluoride solutions by omitting the stage of the preparation of pure Nb_2O_5 or Ta_2O_5.

Experimental Section

Preparation: Reagent grade Nb_2O_5 (Alfa Aesar), Ta_2O_5 and HF (48%, Sigma–Aldrich) were used for the preparation of stock solutions of oxofluoroniobic and fluorotantalic acids. The oxides were suspended in slightly diluted HF (48% HF/H_2O = 2:1) so that the fluorine-to-metal molar ratio became equal to six (for Nb) and seven (for Ta). Both Nb_2O_5 and Ta_2O_5 react with HF already under ambient conditions, but complete dissolution was achieved by treatment for 12 h at 120 °C in Teflon-lined autoclaves. Prior to the syntheses, the concentrations of acids were adjusted to 0.33 M (metal basis) by adding distilled water. Fresh solutions of bases (7 N) were prepared: from dry reagent grade KOH, by dilutioin of NH_3 (36%) and RbOH (50%) and by evaporation of CsOH (50%); all bases were purchased from Alfa Aesar. Two sets of experiments were carried out: very mild (short-time boiling) and hydrothermal. In a typical mild synthesis, oxofluoroniobic or fluorotantalic acid was mixed with a controlled excess amount of alkali (20 mL of 0.33 M acid solution, volume ratios of acid/alkali solutions were chosen as 1:1 for NH_3 and 4:1 for other bases) in a Teflon beaker whilst stirring at room temperature followed by heating on a hot plate and boiling for 15 min. Hydrothermal syntheses were carried out with the same kinds of mixtures in Teflon-lined autoclaves (170 °C, 12 h). The resulting products were washed five times each (distilled water followed by decantation) and air-dried on paper filters at room temperature.

Ion Exchange: Supernatant solutions were prepared by dissolution of reagent grade nitrates of Sr, Ba, Cd, Pb, Co, Ni or Cu (Sigma–Aldrich) in distilled water (1 L). The batches of nitrates were calculated and weighted to attain concentrations of approximately 50 mg/L (δ = 50 ppm) for each cation in 1 L of solution. The measured pH of the prepared solution was equal to 6.7. $NH_4Nb_2O_5(OH,F)$ (sample NH3Nb-B) (100 mg) and $KNb_2O_5F\cdot nH_2O$ (sample KNb-B, 100 mg) were immersed each in supernatant solution (20 mL) in plastic syringes and sustained for 10 h with shaking each hour. After that, an aliquot of clear depleted supernatant (10 mL) was taken off for ICP measurements. Distribution coefficients (K_D, mL/g) were calculated by using the equation:

$$K_D = \frac{V(C_f - C_i)}{mC_f}$$

where V = volume of supernatant solution (mL); m = mass of ion exchanger (g); C_i and C_f = initial and residual concentrations of analyzed ion in supernatant (g/mL).

Characterization: Chemical analyses for all cations were performed by using the ICP method in the labs of Mekhanobr. Ltd. (Saint Petersburg). Fluorine contents in K-, Rb- and Cs-pyrochlores were determined from Nb/F and Ta/F ratios obtained by EDX analysis (CamScan scanning electron microscope with LINK ISIS EDX system); K_2NbF_7 and K_2TaF_7 were used as standards for fluorine. H_2O, NH_3 and HF contents in ammonium pyrochlores were determined by TGA (Netzsch TG 209 F1 thermograph) coupled with a FTIR evolved gas analyzer (Bruker Vertex 70 spectrophotometer with gas analysis chamber and nitrogen-cooled MCT detector). TGA was also used for H_2O determination in K-, Rb- and Cs-pyrochlores. TGA analyses were carried out under an Ar flow of 20 mL/min and included 30 min isothermal staging (30 °C) followed by heating to 1000 °C (10 °/min) and final annealing at 1000 °C for 1 h. FTIR traces of the evolved vapours were integrated in absorption windows of 980–900 cm^{-1} (for NH_3), 1570–1490 cm^{-1} (for H_2O) and 3900–3600 cm^{-1} (for HF). TEM characterization was carried out with FEI Tecnai G^2 300 kV FETEM. X-ray studies were performed by using different diffractometers, depending on the line broadening of powder patterns. A Stoe Stadi P diffractometer [Cu-$K_{\alpha1}$, bent Ge (111) monochromator, transmission geometry, position sensitive detector] was employed for the Rietveld refinements of patterns with mean FWHM < 0.3° (2θ); a Rigaku Miniflex instrument (Cu-K_α, β-filter, Bragg–Brentano geometry) was employed for overview patterns and for the Rietveld refinements when FWHM was between approximately 0.5 and 1.5°; a Stoe IPDS II instrument (Mo-K_α, fine focus tube, graphite monochromator, image plate area detector, flat plate geometry) was used for the Rietveld refinements when FWHM (for Cu-K_α) typically exceeded 1.7° (2θ). Whenever possible, crystal structures were first solved by ab initio methods and refined by the single-crystal approach (SHELX-97),[42] taking $|F_{hkl}|^2$ from integral intensities of 20–22 unambiguously indexed reflections. Integral intensities were measured by use of OPUS 6.5 software (Bruker Optik Gmbh) and then recalculated into $|F_{hkl}|^2$. Final refinements were carried out by the Rietveld method with the FullProf program suite.[43]

Further details on the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-421270 to -421279.

Supporting Information (see footnote on the first page of this article): Chemical composition of the synthesized pyrochlores and Rietveld refinement plots for the samples listed in Table 2.

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