A[Bi₃Ti₄O₁₃] and A[Bi₃PbTi₅O₁₆] (A = K, Cs): New *n* = 4 and *n* = 5 Members of the Layered Perovskite Series, A[A′$_{n-1}$B$_n$O$_{3n+1}$], and Their Hydrates

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We describe the synthesis and structural characterization of new layered bismuth titanates, A[Bi₃Ti₄O₁₃] and A[Bi₃PbTi₅O₁₆] for A = K, Cs, corresponding to *n* = 4 and 5 members of the Dion−Jacobson series of layered perovskites of the general formula, A[A′$_{n-1}$B$_n$O$_{3n+1}$]. These materials have been prepared by solid state reaction of the constituents containing excess alkali, which is required to suppress the formation of competitive Aurivillius phases. Unlike the isostructural niobates and niobium titanates of the same series, the new phases reported here are spontaneously hydrated—a feature which could make them potentially useful as photocatalysts for water splitting reaction. On hydration of the potassium compounds, the *c* axis expands by ca. 2 Å and loses its doubling [for example, the tetragonal lattice parameters of K[Bi₃Ti₄O₁₃] and its dihydrate are respectively *a* = 3.900(1) Å, *c* = 37.57(2) Å; *a* = 3.885(1) Å, *c* = 20.82(4) Å]; surprisingly, the cesium analogues do not show a similar change on hydration.

Introduction

Among the lamellar oxides containing metal−oxygen octahedra,[1] two series consisting of ⟨100⟩ cut perovskite sheets have attracted considerable attention. One is the Ruddlesden−Popper (R−P) series,[2] A₂[A′$_{n-1}$B$_n$O$_{3n+1}$], typified by Sr₂TiO₄ (*n* = 1), Sr₃Ti₂O₇ (*n* = 2), and Sr₄Ti₃O₁₀ (*n* = 3). The other is the more recently discovered Dion−Jacobson (D−J) series,[3,4] A[A′$_{n-1}$B$_n$O$_{3n+1}$]. KLaNb₂O₇ (*n* = 2)[5] and CsCa₂Nb₃O₁₀ (*n* = 3)[3] are representative members of this series. Oxides belonging

to both the structure types exhibit a variety of properties of current interest to materials chemistry.[6] Among the several materials properties, the photodecomposition of water by spontaneously hydrated layered perovskites, A₂La₂Ti₃O₁₀ (A = K, Rb) is a significant new development from the viewpoint of photon energy conversion.[7] The latter series of oxides, which are *n* = 3 members of the R−P series, were synthesized by us some time back.[8] Higher members of this series or the D−J series containing only Ti(IV) in the perovskite sheets are not known, although higher members of the D−J series containing Nb(V) or Nb(V) and Ti(IV) have been reported.[4,9] We investigated the formation of higher members of the titanates. We could not however prepare higher (*n* ≥ 4) members of the titanate series such as K₂La₂CaTi₄O₁₃ and KLa₃Ti₄O₁₃ by conventional methods, probably because of the volatility of potassium at the high reaction temperatures (>1300 °C) required for their synthesis. We attempted to prepare similar bismuth/lead titanates such as K₂Bi₂Ti₃O₁₀, K₂Bi₂PbTi₄O₁₃, and KBi₃Ti₄O₁₃, which we expected would form at relatively low temperatures. Here again we did not obtain the desired phases in view of the overwhelming stability of the Aurivillius phases,[10] Bi₄Ti₃O₁₂ and PbBi₄Ti₄O₁₅, which were formed as major products from stoichiometric reaction mixtures. We could however obtain the desired phases starting from reaction mixtures that contained a considerable excess of the alkali component; excess alkali was required not only to bring down the reaction temperature but also to suppress the formation of competitive Aurivillius phases.[10] By using this strategy, we have prepared and characterized several new members of the D−J series, A[Bi₃-

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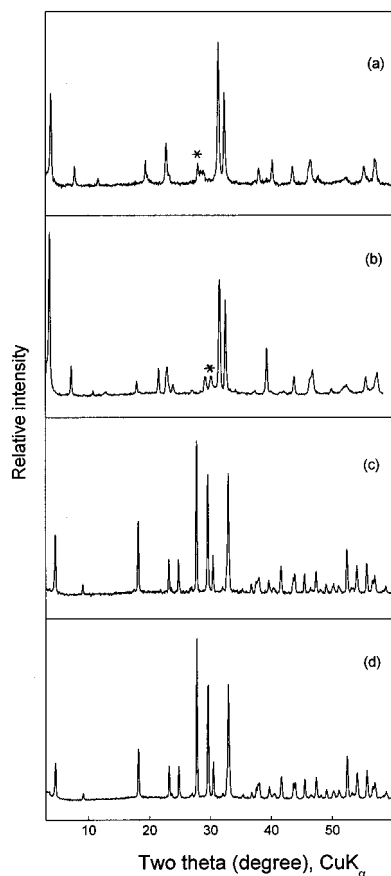
Table 1. Powder XRD Data for $K[Bi_3Ti_4O_{13}]$ and Its Hydrate

$K[Bi_3Ti_4O_{13}]^a$						$K[Bi_3Ti_4O_{13}]\cdot 2H_2O^b$					
h	k	l	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	h	k	l	d_{obs} (Å)	d_{cal} (Å)	I_{obs}
0	0	2	18.750	18.785	88	0	0	1	20.710	20.820	100
0	0	4	9.372	9.394	20	0	0	2	10.384	10.408	15
0	0	8	4.700	4.697	22	0	0	3	6.920	6.940	9
1	0	1	3.873	3.880	47	0	0	4	5.200	5.204	17
1	0	7	3.160	3.156	50	0	0	5	4.160	4.163	17
1	0	9	2.850	2.850	100	1	0	0	3.880	3.885	27
1	1	0	2.752	2.760	68	1	0	1	3.815	3.819	18
1	1	8	2.375	2.378	20	1	0	4	3.113	3.113	23
1	0	13	2.305	2.321	15	0	0	7	2.962	2.973	26
1	1	10	2.225	2.224	23	1	0	5	2.842	2.840	58
0	0	18	2.087	2.087	18	1	1	0	2.742	2.747	48
2	0	0	1.951	1.950	35	1	1	4	2.429	2.429	10
2	1	1	1.743	1.743	18	1	1	5	2.296	2.293	25
1	1	18	1.667	1.665	22	1	1	6	2.146	2.154	10
2	1	9	1.609	1.609	26	0	0	10	2.082	2.082	14
2	1	15	1.429	1.431	15	1	0	9	1.986	1.987	11
2	2	0	1.378	1.379	15	2	0	0	1.942	1.942	23
						2	0	5	1.759	1.760	12
						1	1	10	1.659	1.659	13
						2	1	5	1.604	1.603	18
						2	0	10	1.420	1.420	10
						2	2	1	1.370	1.370	9

^{a} $a = 3.900(1)$ Å, $c = 37.57(2)$ Å. ^{b} $a = 3.885(1)$ Å, $c = 20.82(4)$ Å.

Figure 1. Powder XRD patterns of (a) $K[Bi_3PbTi_5O_{16}]$, (b) $K[Bi_3PbTi_5O_{16}]\cdot 2H_2O$, (c) $Cs[Bi_3Ti_4O_{13}]$, and (d) $Cs[Bi_3Ti_4O_{13}]\cdot H_2O$. Reflections due to an unidentified impurity phase are marked by asterisks.

$Ti_4O_{13}]$ and $A[Bi_3PbTi_5O_{16}]$ (A = K, Cs) and their hydrates. We describe the results of these investigations in this paper.

Experimental Section

K_2CO_3/KNO_3, Bi_2O_3, and TiO_2 (together with yellow PbO where required) were mixed corresponding to the compositions of $n = 3, 4$, and 5 members of the R–P series (viz., $K_2Bi_2Ti_3O_{10}$, $K_2Bi_{2.5}K_{0.5}Ti_4O_{13}$, $K_2Bi_2PbTi_4O_{13}$, and $K_2Bi_3KTi_5O_{16}$) and reacted at elevated temperatures (750–1000 °C) for various duration in air or argon. Excess K_2CO_3/KNO_3 was also added in several preparations to compensate for potassium loss due to volatilization. The products were examined at various stages of the reaction by powder X-ray diffraction (XRD) using a Siemens D-5005 powder diffractometer (Cu Kα radiation). Final products were washed with distilled water and dried at 110 °C in an air oven. Potassium contents of the single-phase products were determined by flame photometry. The metallic elemental ratios were also determined by EDX analysis (JEOL JSM 840A). The hydration behavior of the single-phase materials was investigated by thermogravimetry (Cahn TG131 system, 2°/min). The structures of the single-phase materials were also investigated by electron diffraction (JEOL JEM 200-CX transmission electron microscope). Having established the compositions of the single-phase materials formed in the K–Bi (Pb)-Ti–O system, we carried out similar investigations with Cs–Bi (Pb)-Ti–O system to prepare the cesium analogues.

Results and Discussion

Reaction of K_2CO_3, Bi_2O_3 (PbO), and TiO_2 taken in various stoichiometric proportions corresponding to $n = 3, 4$, and 5 members of the R–P series revealed that a $n = 4$-like material was formed at 750 °C/6 h, while a $n = 5$-like material was
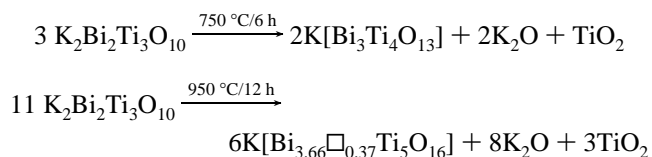
obtained at 950 °C/12 h. The characteristic 00*l* reflections corresponding to the $n = 4$ phase were seen in the XRD patterns at $d \simeq 19.0, 9.4, 6.3$, and 4.7 Å; similar 00*l* reflections for the $n = 5$ phase were seen at $d \simeq 23.0, 11.5, 7.6$, and 5.1 Å. Significantly, in none of the preparations did we find evidence for the formation of a $n = 3$ phase similar to $K_2La_2Ti_3O_{10}$.[8] By optimizing the reaction temperature and duration of reaction, we could obtain nearly single-phase $n = 4$ and 5 phases at 750 °C/6 h and 950 °C /12 h in air followed by washing the reaction products with distilled water.

Chemical analysis by flame photometry revealed that the potassium contents (3.50% and 3.00%) of the $n = 4$ and 5 phases were more close to the values expected for the formulations $K[Bi_3Ti_4O_{13}]$ ($K = 3.67\%$) and $K[Bi_{3.66}Ti_5O_{16}]$ ($K = 3.01\%$) than the formulations $K_2Bi_{2.5}K_{0.5}Ti_4O_{13}$ ($K = 9.61\%$) and $K_2Bi_3KTi_5O_{16}$ ($K = 9.46\%$). Accordingly, we believe that the $n = 4$ and $n = 5$ members prepared by us were members of the D–J series,[3,4] $K[A_{n-1}B_nO_{3n+1}]$, and not members of the R–P series.[2] The formation of these $n = 4$ and $n = 5$ phases starting from the nominal $K_2Bi_2Ti_3O_{10}$ reaction mixture could be written as follows:

$$3\ K_2Bi_2Ti_3O_{10} \xrightarrow{750\ °C/6\ h} 2K[Bi_3Ti_4O_{13}] + 2K_2O + TiO_2$$

$$11\ K_2Bi_2Ti_3O_{10} \xrightarrow{950\ °C/12\ h}$$
$$6K[Bi_{3.66}\square_{0.37}Ti_5O_{16}] + 8K_2O + 3TiO_2$$

Having identified the compositions of the new phases, we attempted to prepare these materials by reacting stoichiometric mixtures of the oxides and K_2CO_3 corresponding to the compositions, $K[Bi_3Ti_4O_{13}]$ ($n = 4$) and $K[Bi_{3.66}Ti_5O_{16}]$ ($n = 5$). Surprisingly, however, we did not obtain the expected products; instead, the products contained $Bi_4Ti_3O_{12}$, an $n = 3$ member of the Aurivillius series,[10] $(Bi_2O_2)\ [A_{n-1}B_nO_{3n+1}]$, as the major phase.
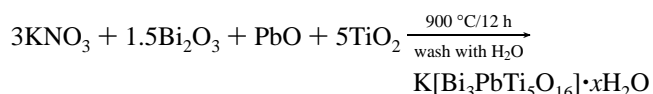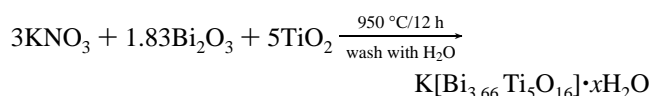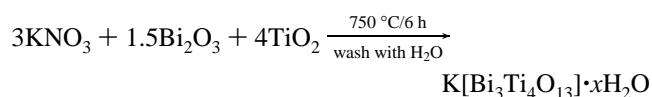
Then, we realized that excess of potassium content in the reaction mixture is required to suppress the formation of the stable Aurivillius phase. Indeed, when we started with mixtures

Table 2. Chemical Compositions, Synthetic Methods, and Lattice Parameters of Layered Perovskite Titanates $A[Bi_3Ti_4O_{13}]$ and $A[Bi_3PbTi_5O_{16}]$ (A = K, Cs) and Their Derivatives

composition	details of synthesis	lattice parameters (Å)	
		a	*c*
$K[Bi_3Ti_4O_{13}] \cdot 2H_2O$	$3KNO_3 + 1.5Bi_2O_3 + 4TiO_2$; heated at 750 °C for 6 h; product washed with distilled water, dried at 110 °C	3.885(1)	20.82(4)
$K[Bi_3Ti_4O_{13}]$	$KBi_3Ti_4O_{13} \cdot 2H_2O$; dehydrated at 400 °C for 30 min in air	3.900(1)	37.57(2)
$K[Bi_3PbTi_5O_{16}] \cdot 2H_2O$	$3KNO_3 + 1.5Bi_2O_3 + PbO + 5TiO_2$; heated at 900 °C for (6 + 6)h; product washed with distilled water, dried at 110 °C	3.893(2)	24.78(1)
$K[Bi_3PbTi_5O_{16}]$	$KBiPbTi_5O_{16} \cdot 2H_2O$; dehydrated at 400 °C for 30 min in air	3.914(1)	45.65(2)
$K[Bi_{3.66}Ti_5O_{16}] \cdot 4H_2O$	$3KNO_3 + 1.83Bi_2O_3 + 5TiO_2$; heated at 950 °C for 12 h; product washed with distilled water, dried in air	3.907(2)	25.06(2)
$K[Bi_{3.66}Ti_5O_{16}]$	$K[Bi_{3.66}Ti_5O_{16}] \cdot 4H_2O$ dehydrated at 400 °C for 30 min in air	3.918(2)	45.52(7)
$Cs[Bi_3Ti_4O_{13}] \cdot H_2O$	$3CsNO_3 + 1.5Bi_2O_3 + 4TiO_2$; heated at 750 °C for 6 h; product washed with distilled water, dried over $CaCl_2$ in a desiccator	7.685(1)	38.99(1)
$Cs[Bi_3Ti_4O_{13}]$	$CsBi_3Ti_4O_{13} \cdot H_2O$; dehydrated at 400 °C for 30 min in air	7.685(1)	38.99(1)
$Cs[Bi_3PbTi_5O_{16}] \cdot 2.5H_2O$	$3CsNO_3 + 1.5Bi_2O_3 + PbO + 5TiO_2$; heated at 900 °C for 12 h; product washed with distilled water, dried over $CaCl_2$ in a desiccator	7.712(1)	46.86(2)
$Cs[Bi_3PbTi_5O_{16}]$	$CsBiPbTi_5O_{16} \cdot 2.5H_2O$; dehydrated at 400 °C for 30 min in air	7.712(1)	46.86(2)
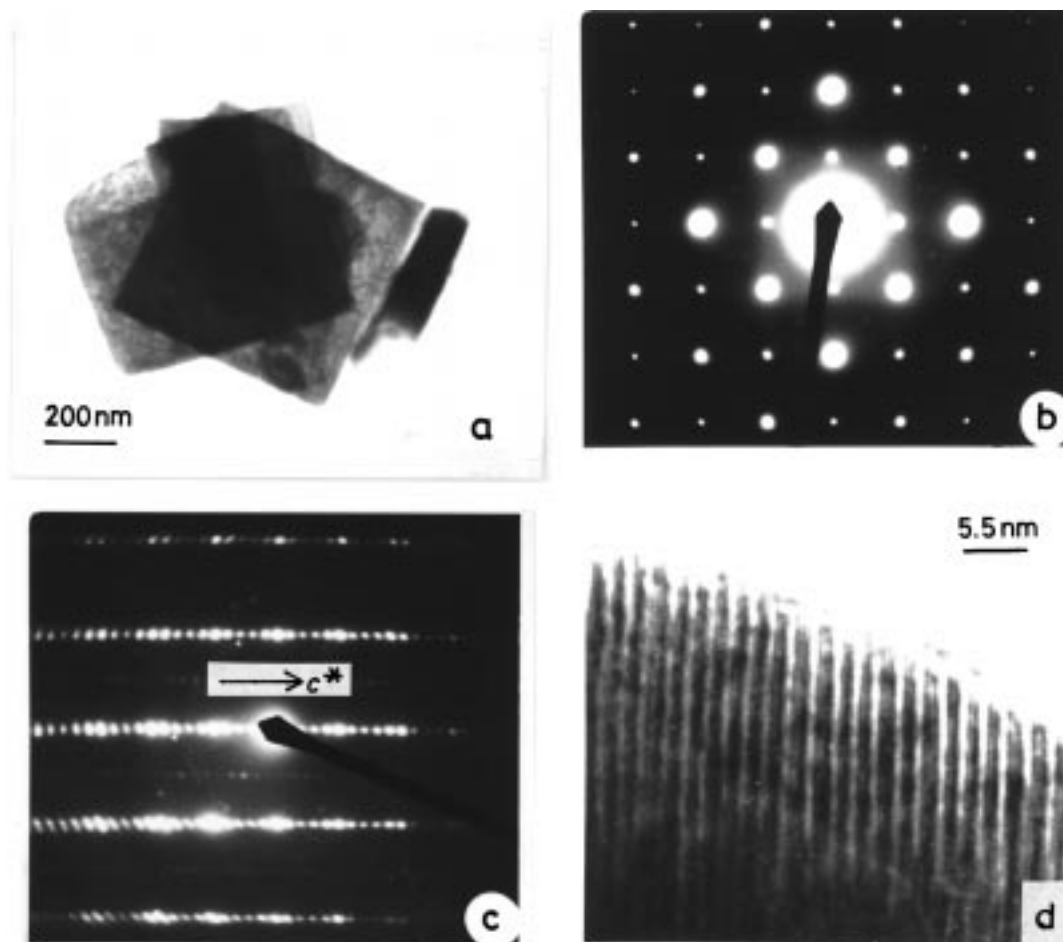
Figure 2. Electron diffraction (ED) data for $K[Bi_3Ti_4O_{13}]$. (a) Bright field image showing cubic platelet morphology of the crystals. (b) Selected area ED pattern recorered with [001] beam direction showing a perovskite cell ($a_p \simeq 3.9$ Å) in the *ab* plane. (c) ED pattern recorded with [010] beam direction showing *ca.* 18.5 Å periodicity along *c**. In (d), the lattice image corresponding to the diffraction pattern (c) is shown, revealing the presence of *ca.* 18.5 Å lattice fringes.

containing excess (2 mol) of alkali, we obtained the desired single-phase products. Subsequently, we found that using KNO_3 instead of K_2CO_3 as the alkali source yielded better results. Accordingly, we standardized the conditions for the preparation of single-phase *n* = 4 and *n* = 5 members as follows:

$$3KNO_3 + 1.5Bi_2O_3 + 4TiO_2 \xrightarrow[\text{wash with H}_2\text{O}]{750\ °\text{C}/6\ \text{h}}$$
$$K[Bi_3Ti_4O_{13}] \cdot xH_2O$$

$$3KNO_3 + 1.83Bi_2O_3 + 5TiO_2 \xrightarrow[\text{wash with H}_2\text{O}]{950\ °\text{C}/12\ \text{h}}$$
$$K[Bi_{3.66}Ti_5O_{16}] \cdot xH_2O$$

$$3KNO_3 + 1.5Bi_2O_3 + PbO + 5TiO_2 \xrightarrow[\text{wash with H}_2\text{O}]{900\ °\text{C}/12\ \text{h}}$$
$$K[Bi_3PbTi_5O_{16}] \cdot xH_2O$$

TG analysis revealed that the products were hydrated and the water of hydration varied with drying condition. For samples

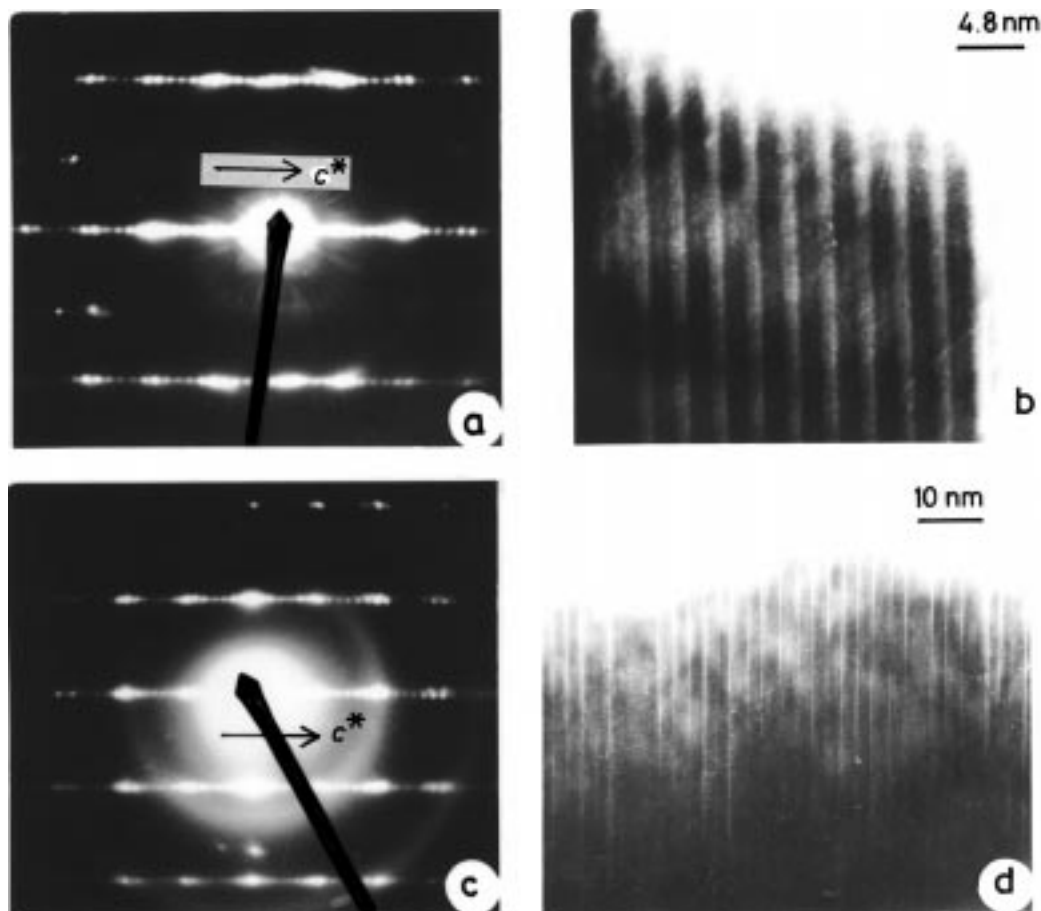**Figure 3.** Electron diffraction (ED) data for K[Bi$_3$PbTi$_5$O$_{16}$] and K[Bi$_{3.66}$Ti$_5$O$_{16}$]. (a) ED pattern of K[Bi$_3$PbTi$_5$O$_{16}$] recordered with [010] beam direction showing ca. 23 Å periodicity along c^*. (b) Lattice image corresponding to the ED pattern shown in (a), revealing the presence of ca. 23 Å lattice fringes. In (c) and (d), the corresponding data for K[Bi$_{3.66}$Ti$_5$O$_{16}$] are shown.

dried at 110 °C, the water of hydration for $n = 4$ and 5 phases is 2H$_2$O. Chemical analysis of the potassium contents by flame photometry were consistent with the formulas given above. The KTiBi atomic percentages determined by EDX analysis for anhydrous K[Bi$_3$Ti$_4$O$_{13}$] (12.81:50.13:37.06) were also in agreement with the expected values (12.50:50.00:37.50) calculated for 1K3Bi4Ti.

We show in Figure 1 typical powder XRD patterns of the hydrated and anhydrous titanates, and in Table 1 we give indexing of the powder XRD data for a representative member K[Bi$_3$Ti$_4$O$_{13}$] and its hydrate. In Table 2, we summarize the tetragonal lattice parameters of all the new phases synthesized by us. It must be mentioned that the c parameters of the anhydrous $n = 4$ and 5 members are comparable to the c-parameters of similar $n = 4$ and 5 members of the niobate series, K[Ca$_2$Na$_{n-3}$Nb$_n$O$_{3n+1}$], reported by Dion et al.[3] and Jacobson et al.[4] The layered titanates reported here are spontaneously hydrated taking up 2−4 molecules of water per formula unit. On drying at 110 °C, a stable dihydrate is obtained. We see (Table 2) that, on hydration, not only is there an expansion of the c axis by ca. 2 Å (per perovskite slab) for the dihydrate, but also halving of the c periodicity. While the corresponding niobium and niobium−titanium oxides of the D−J series do not show such a hydration behavior,[4,9] members of the R−P series, K$_2$Ln$_2$Ti$_3$O$_{10}$ (Ln = La, Nd) do exhibit a similar hydration behavior.[8,11,12] The β modification of NaCa$_2$Nb$_3$O$_{10}$ has however been reported to form a hydrate.[6a]

To characterize the layered structure of the potassium titanates, we have recorded the electron diffraction patterns and high-resolution lattice images for the $n = 4$ and 5 members (Figures 2 and 3). We see that all the samples are crystalline showing typical perovskite cell ($a_p \sim 3.9$ Å) patterns in the [001] beam direction. When the beam direction is along [010], we see clear evidence for *ca.* 18.5 and *ca.* 23 Å repeat in the c^* direction for the $n = 4$ and 5 members, respectively. We also see lattice fringes with the same repeats (corresponding to $^1/_2c$) in the lattice images (Figures 2d and 3b). Interestingly, for the $n = 5$ member, K[Bi$_{3.66}$Ti$_5$O$_{16}$], both ED patterns and lattice images show considerable disorder in the c direction (Figure 3c and d), revealing the presence of perovskite sheets of variable thickness in addition to the $n = 5$ sheets. We show schematically in Figure 4 the idealized structures of K[Bi$_3$Ti$_4$O$_{13}$] and K[Bi$_3$PbTi$_5$O$_{16}$]. It must be mentioned that both the potassium compounds readily undergo K$^+$/H$^+$ exchange in aqueous acid (3 N HNO$_3$) at room-temperature yielding the protonated analogues, similar to the isostructural niobium and niobium−titanium members of the D−J series.[3,4,9] Further investigations of the protonated phases to characterize their Brønsted acidity and intercalation chemistry are in progress.

In an effort to characterize the formation of similar layered perovskite titanates with other alkali metals, we investigated the formation of Cs[Bi$_3$Ti$_4$O$_{13}$] ($n = 4$) and Cs[Bi$_3$PbTi$_5$O$_{16}$] ($n = 5$). We could readily prepare these phases by reacting the stoichiometric constituents containing excess (2 mol) of CsNO$_3$ in air. The $n = 4$ member was obtained at 750 °C/6 h and the

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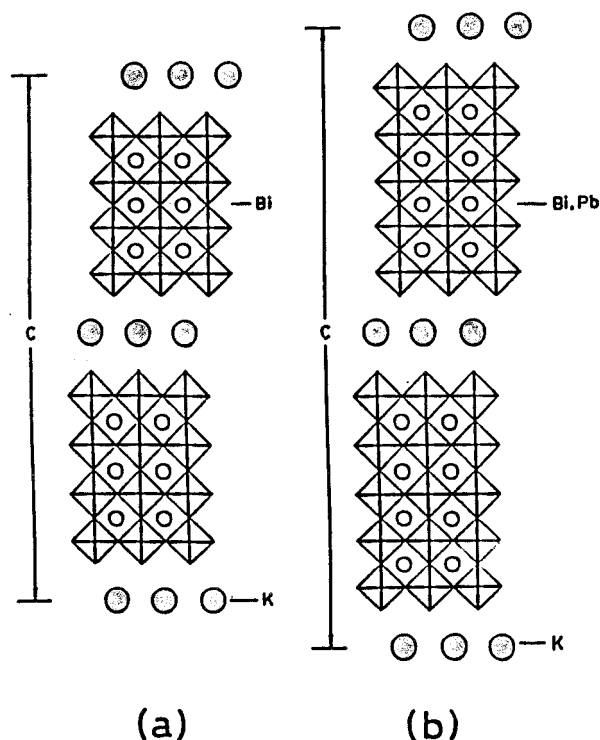
Figure 4. Schematic structures of (a) K[Bi$_3$Ti$_4$O$_{13}$] and (b) K[Bi$_3$-PbTi$_5$O$_{16}$].

$n = 5$ member at 900 °C/12 h. The single-phase materials, obtained by washing the reaction products with distilled water and drying over CaCl$_2$ in a desiccator, were found to be hydrated containing 1−2.5 molecules of water. Surprisingly, the powder XRD patterns of both the anhydrous and hydrated phases were nearly the same (Figure 1 and Table 2) indicating no apparent structural change on hydration. We list the lattice parameters of both the anhydrous and hydrated phases in Table 2.

In conclusion, we have prepared new layered perovskite titanates of the formulas, K[Bi$_3$Ti$_4$O$_{13}$], K[Bi$_{3.66}$Ti$_5$O$_{16}$], and K[Bi$_3$PbTi$_5$O$_{16}$], starting from stoichiometric reaction mixtures containing excess alkali. These oxides correspond to $n = 4$ and $n = 5$ members of the Dion−Jacobson series of layered perovskite oxides of the general formula, A[A′$_{n-1}$B$_n$O$_{3n+1}$]. Excess alkali is required not only to suppress the formation of the competitive Aurivillius phases but also to bring down the reaction temperature for the formation of the desired phases. We could also prepare the corresponding cesium analogues by the same method. All these layered titanates are spontaneously hydrated − a feature which is likely to be important for use of these materials as photocatalysts in the water splitting reaction.

Supporting Information Available: Figure S1 showing thermogravimetric data and Tables S1 and S2 giving powder XRD data of layered titanates reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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