Materials Research Bulletin 46 (2011) 398–406

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

New solid acids in the triple-layer Dion–Jacobson layered perovskite family

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ARTICLE INFO

Article history:
Received 27 July 2010
Received in revised form 24 November 2010
Accepted 3 December 2010
Available online 10 December 2010

Keywords:
A. Layered compounds
A. Oxides
B. Intercalation reactions
C. Thermogravimetric analysis (TGA)
C. X-ray diffraction

ABSTRACT

Dion–Jacobson type layered perovskites such as $A'Ca_2Nb_3O_{10}$ (A′ = K, Rb, H) have continued to be of great interest due to their compositional variability, rich interlayer chemistry, and wide range of physical properties. In this study, we investigated the range and effects of substitutional doping of Ta^{5+} for Nb^{5+} and of Sr^{2+} for Ca^{2+} in $A'Ca_2Nb_3O_{10}$. We have prepared and characterized three new solid solutions: $KCa_2Nb_{3-x}Ta_xO_{10}$, $RbCa_2Nb_{3-x}Ta_xO_{10}$, and $RbCa_{2-x}Sr_xNb_3O_{10}$. These materials all readily undergo proton exchange to form two new series of hydrated solid acid phases, which in most cases can be dehydrated to form stable $HCa_2Nb_{3-x}Ta_xO_{10}$ and $HCa_{2-x}Sr_xNb_3O_{10}$ compounds. Intercalation studies with *n*-hexylamine and pyridine were carried out to gauge the relative Brønsted acidities across the $HCa_2Nb_{3-x}Ta_xO_{10}$ series, and we determined that materials with the highest tantalum contents are weaker acids than the parent compound $HCa_2Nb_3O_{10}$. Preliminary intercalation studies with pyridine for the $HCa_{2-x}Sr_xNb_3O_{10}\cdot yH_2O$ solid acids, however, showed no significant difference in acidity with varying strontium content.

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1. Introduction

The extraordinary versatility of the perovskite structure is well known in solid state and materials chemistry. The related family of structures known collectively as layered perovskites is proving to be equally capable of accommodating variations in chemical composition. Two main classifications of layered perovskites are the Ruddlesden–Popper-type phases [1,2], typified by $K_2La_2Ti_3O_{10}$ [3] and the Dion–Jacobson-type phases such as $KCa_2Nb_3O_{10}$ [4,5]. Several excellent reviews of the structures, properties [6], and reaction chemistry [7,8] of layered perovskites have been compiled. These materials exhibit a wide range of properties depending on composition including superconductivity [9–13], ionic conductivity [14–17], dielectric behavior [18], luminescence [19–21], colossal magnetoresistance [22,23], and photocatalytic activity [24–27]. Interest in photocatalysis continues to drive a great deal of research on the Dion–Jacobson layered perovskites, in part due to their rich interlayer chemistry and band gap tunability.

Dion–Jacobson-type layered perovskites can be represented with the general formula $A'[A_{n-1}B_nO_{3n+1}]$. The monovalent A′ cations reside between negatively charged $[A_{n-1}B_nO_{3n+1}]$ perovskite-type layers composed of corner-shared BO_6 octahedra that are *n* octahedra thick; most commonly, the B cations are titanium, niobium or tantalum. When the Dion–Jacobson phases are prepared at high temperatures, the A′ cations are usually the larger alkali metal ions (K^+, Rb^+, or Cs^+), but these can undergo ion exchange under *chimie douce* conditions to obtain phases with a wide diversity of monovalent cations including protons [5,28,29]. The protonated phases behave as solid acids and readily intercalate a variety of amines spreading the perovskite layers even further apart, depending on the amine [30]. In some cases if the amine is bulky enough, intercalation results in exfoliation of the perovskite layers, forming colloidal suspensions of nanosheets [31]. These nanosheets can then be restacked to form thin films and unique multilayer structures [32,33]. The use of restacked nanosheets enhances the photocatalytic activity over bulk materials and allows for facile deposition of co-catalysts within the interlayer region [34–37]. Maeda and Mallouk recently reported a study comparing the photocatalytic activity of double-layer and triple-layer, restacked Dion–Jacobson-type nanosheets, highlighting for the first time, several important structural and electronic features that lead to high photocatalytic activity [38].

Although the band gap energies of the niobate and tantalate Dion–Jacobson phases lie in the ultraviolet region, the amenability of the layered perovskite to chemical substitution has led to several strategies for lowering the band gap energy into the visible region in order to make more efficient photocatalysts. For example, Schottenfeld et al. used ammonialysis to convert $RbCa_2Nb_3O_{10}$ and $RbLaNb_2O_7$ into oxynitride phases that absorbed in the visible region, but these were poor photocatalysts due to their instability

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doi:10.1016/j.materresbull.2010.12.007

in water [39]. Substitution of lead resulted in visible-light induced photocatalytic activity in $RbPb_2Nb_3O_{10}$ [40] and has been suggested as a general strategy to sensitize these types of materials in the visible region [41]. The flurry of research in recent years, particularly in the area of photocatalysis, indicates that the Dion–Jacobson layered perovskites continue to show great promise as a versatile and highly tunable class of materials. In this paper, we expand upon the range of compositions that are known by synthesizing and characterizing two new solid solution families, $MCa_2Nb_{3-x}Ta_xO_{10}$ (M = K, Rb, H) and $MCa_{2-x}Sr_xNb_3O_{10}$ (M = Rb, H). Although the end members of these solid solutions are known, the intermediate compositions and their proton-exchange products are largely unknown. We believe that in particular, the protonated solid solutions may prove to be interesting and potentially useful building blocks to new functional materials.

Prior studies on the solid solution behavior of Dion–Jacobson layered perovskites have largely focused on the impact of composition on the relative acidities of the protonated phases. For example, several reports have explored the effects of transition metal ion doping on the B-site of $HCa_2Nb_3O_{10}$, substituting Ti^{4+}, Fe^{3+}, or Al^{3+} in place of Nb^{5+}. Chemical substitution on the B-site should directly impact the relative acidities due to the fact that the protons are bonded to the outer layer BO_6 octahedra and changes in the B–O bond strength will also affect the O–H bond strength. Gopalakrishnan et al. were the first to examine the relative acidities of $HCa_{2-x}La_xNb_{3-x}Ti_xO_{10}$ as a function of Ti^{4+} content [42]. Based on amine intercalation studies, they proposed an ordering of Ti^{4+} and Nb^{5+} in the triple-layer perovskite slabs such that $HCaLaNb_2TiO_{10}$ with Ti^{4+} sequestered in the central layer of octahedra and not bound to protons was nearly as acidic as the parent $HCa_2Nb_3O_{10}$, whereas $HLa_2NbTi_2O_{10}$ with Nb^{5+} in the central octahedra and Ti^{4+} in the outer octahedra exhibited weaker Brønsted acidity for the protons attached to TiO_6 octahedra. Later studies [43] established a more complex ordering scheme for Ti^{4+}/Nb^{5+} ions that retained some NbO_6 in the outer octahedra for $HLa_2NbTi_2O_{10}$ and in contrast to Gopalakrishnan, Hong et al. were able to observe the intercalation of n-alkylamines in $HLa_2NbTi_2O_{10}$, indicating a similar acidity to $HCa_2Nb_3O_{10}$. This new B-site ordering scheme was also confirmed in $RbLa_2Ti_2NbO_{10}$ [44] and $MLa_2Ti_2TaO_{10}$ (M = Cs, Rb) [45], although the impact on the relative Brønsted acidity of $HLa_2Ti_2TaO_{10}$ was unclear since amine intercalation results seemed to be highly dependant on reaction conditions [46]. Uma and Gopalakrishnan also examined the relative acidities of $HCa_2Nb_{3-x}M_xO_{10-x}$ (M = Al, Fe) as the trivalent ions Al^{3+} and Fe^{3+} substituted for Nb^{5+} in the perovskite slabs [47]. They proposed that interlayer protons attached to AlO_6 or FeO_6 octahedra were less acidic than those attached to NbO_6 octahedra, confirmed by the decreasing amount of intercalated amines as the aluminum or iron content increased. Later work suggested the extent of aluminum and iron doping is limited in these phases as $CsCa_2Nb_2AlO_9$ and $CsCa_2Nb_2FeO_9$ were actually multi-phase mixtures of 2D layered perovskites and 3D perovskites [48].

We initially began our investigations of the $HCa_2Nb_{3-x}Ta_xO_{10}$ solid solution family motivated by these studies of B-site substitution and relative acidity. Rather than focusing on substitution of ions with different charges, we chose to examine the effects of varying B–O bond strengths for two ions with the same charge, namely Nb^{5+} and Ta^{5+}. To characterize the relative acidities of $HCa_2Nb_{3-x}Ta_xO_{10}$, we have carried out intercalation reactions across the series with n-hexylamine and pyridine and characterized the products by X-ray powder diffraction and thermogravimetric analysis. We have also examined the role of A-site substitution by synthesizing $RbCa_{2-x}Sr_xNb_3O_{10}$ and characterizing the proton exchange chemistry across the solid solution.

2. Experimental

2.1. General

$CaCO_3$ (Mallinckrodt, analytical grade), $SrCO_3$ (Alfa Aesar, 99%), Nb_2O_5 (Cerac, 99.95%, −325 mesh), and Ta_2O_5 (Alfa Aesar, 99.85%, −325 mesh) were used without further purification. Rb_2CO_3 (Alfa Aesar, 99%) and K_2CO_3 (Mallinckrodt, anhydrous) were stored in a drying oven at 120 °C prior to use. Pyridine (Aldrich, anhydrous, 99.8%), n-hexylamine (Aldrich, 99%), heptane (Burdick Jackson, HPLC grade), and concentrated HCl (Fisher, ACS reagent grade) were used as received. X-ray powder diffraction data were collected on a Scintag XDS-2000 diffractometer using Cu Kα radiation (λ = 1.5418 Å), typically from 2 to 70° 2θ and scan rates of 0.1°/min. Diffraction patterns were indexed and lattice parameters were fit using the program Unit Cell [49]. Thermogravimetric analysis was carried out using a Perkin Elmer TGA 7 under flowing O_2, typically from 25 to 900 °C at heating rates of 10°/min.

2.2. Synthesis of parent layered perovskite phases

The alkali metal parent layered perovskite phases were prepared by traditional solid state synthesis routes from stoichiometric mixtures of the appropriate metal oxides and carbonates and a 50% molar excess of the alkali metal carbonate (either Rb_2CO_3 or K_2CO_3) to compensate for the volatility of the alkali metals at high temperatures. Typically, samples were prepared in 2 g batches and reactants were ground and pressed into 1 in. diameter pellets prior to firing in alumina labware. Potassium phases, $KCa_2Nb_{3-x}Ta_xO_{10}$ ($0 \leq x < 3$), were fired at 1200 °C for at least 24 h, often longer with intermittent regrinding in order to obtain single-phase products. The rubidium solid solutions, $RbCa_2Nb_{3-x}Ta_xO_{10}$ ($0 \leq x \leq 3$) and $RbCa_{2-x}Sr_xNb_3O_{10}$ ($0 \leq x \leq 2$), were readily obtained as single-phase samples provided reaction mixtures were first fired at lower temperatures (700–800 °C) for 12–18 h followed by reaction at higher temperatures (1100–1150 °C) for an additional 24–36 h.

2.3. Proton exchange reactions

In a typical proton exchange reaction, up to 4.50 g of the parent alkali metal layered perovskite was combined with 150 mL of 6 M HCl, and the mixture was heated with stirring at 60–80 °C for 3–5 days. The protonated layered perovskite was isolated by filtration, washed with deionized water until the filtrate was a neutral pH, and either left to dry at room temperature to obtain the hydrated phase or dehydrated by heating for several days at 120 °C.

2.4. Amine intercalation reactions

Amine intercalation reactions were carried out by stirring and heating the dehydrated, protonated layered perovskite powder under N_2 with a 100 times molar excess of the amine in solution. Reactions with n-hexylamine or pyridine in heptane (10%, v/v solutions) were heated at reflux temperature (b.p. = 98 °C) for 5–20 days. For long reaction times, the amine solution was replaced every few days. In the case of $HCa_2Nb_{0.5}Ta_{2.5}O_{10}$ and $HCa_2Ta_3O_{10}$, the pyridine reaction was also attempted in neat pyridine; 0.50 g of the protonated layered perovskite was stirred and heated to reflux with 40 mL pyridine (b.p. = 115 °C) under N_2 for 20 days. In all cases, after cooling the reaction mixture, the solids were filtered, washed with heptane, and allowed to dry at room temperature.

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