



Thermal stability and high temperature polymorphism of topochemically-prepared Dion–Jacobson triple-layered perovskites



Stephen L. Guertin, Elisha A. Josepha, Dariush Montasserasadi, John B. Wiley*

Department of Chemistry and Advanced Materials Research Institute, University of New Orleans, 2000 Lakeshore Dr., New Orleans, LA 70148, USA

ARTICLE INFO

Article history:

Received 4 May 2015

Accepted 5 June 2015

Available online 10 June 2015

Keywords:

Oxide materials

Preferential site ordering

Phase transitions

Calorimetry

X-ray diffraction

ABSTRACT

The thermal stability of six Dion–Jacobson-related triple layered perovskites, $ACa_2Nb_3O_{10}$ ($A = H, NH_4, Li, Na, K, CuCl$), was explored to 1000 °C. Each compound was produced topochemically by low-temperature (<500 °C) ion exchange from $RbCa_2Nb_3O_{10}$. The thermal behavior of the series was examined by variable temperature X-ray powder diffraction experiments in tandem with thermogravimetric analysis and differential scanning calorimetry. Five of the species were found to be low temperature/metastable phases, decomposing below 900 °C, where the stability of the series decreased with decreasing interlayer cation size. The compounds, $A = Li, Na, K$, exhibited high temperature polymorphism, with a completely reversible transition evident for $KCa_2Nb_3O_{10}$.

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1. Introduction

Layered perovskite compounds have been extensively studied due to their wide-ranging potential for applications, as well as for their susceptibility to soft chemical manipulation [1–4]. Many high temperature superconductors (e.g., $YBa_2Cu_3O_7$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$) share perovskite-related structures [5–7], and layered perovskite materials have been variously utilized in photocatalysts [8–11], hydrogen sensors [12–14], and fatigue-free capacitors [15–18]. Such materials offer a great versatility with respect to solid state synthesis, allowing important electronic and ferroic properties to be tailored with convenience and ease [4]. Nanostructuring of related perovskites is another exciting new area of research [19].

Soft chemistry (*chimie douce*) involves the use of low-temperature synthetic methods to form desired products that cannot be prepared by traditional high temperature ceramic techniques. For many compounds, one-step, direct synthesis from simple precursors is thermodynamically unfavored. In such cases, soft chemical topotactic routes such as ion exchange and intercalation may be used to retain resilient structural features of a precursor in the products. The strata in layered perovskite oxides can be utilized in this manner to create families of metastable materials

with variant interlayer chemistry [20]. These can, in turn, be used as secondary reagents in multistep synthesis [3].

Layered perovskites of the Dion–Jacobson (DJ) family have the general formula $A[A'_{n-1}B_nO_{3n+1}]$, where typically $A =$ alkali metal, $A' =$ rare earth or alkaline-earth, $B =$ transition metal, and $n =$ number of perovskite layers. This family has been well characterized, including reports on their structures [21–25], electronics [26–28], and magnetism [23,29,30]. In the case of a doped potassium variant, superconductive properties have been observed [31].

The utility and development of topochemical reaction strategies in part relies on determining the effective window of thermal stability for the reagents and intermediates. By defining the limits of these systems and their modifications, strategies can be designed to more effectively access target materials. Recent studies have examined the stability of double-layered perovskites [32,33]. Of the triple-layered species, only $HCa_2Nb_3O_{10}$ and $NaCa_2Nb_3O_{10}$ have been explicitly probed above 500 °C [23,34]. In the research reported herein, the thermal stability of the Dion–Jacobson perovskite series $ACa_2Nb_3O_{10}$ ($A = H, NH_4, Li, Na, K, CuCl$) was investigated. These species can be categorized into three classes based on relative thermal stability and similarity of rearrangement/decomposition pathways. Most interestingly, members of the class $ACa_2Nb_3O_{10}$ ($A = Li, Na, K$) were discovered to undergo endothermic rearrangement into high temperature polymorphs, only one of which has been previously identified [23, 38].

* Corresponding author.

E-mail address: jwiley@uno.edu (J.B. Wiley).

2. Experimental

2.1. Synthesis

RbCa₂Nb₃O₁₀ was synthesized by solid state reaction. Rb₂CO₃ (Alfa Aesar, 99.8%), CaCO₃ (Alfa Aesar, 99.99%), and Nb₂O₅ (Alfa Aesar, 99.9985%) were finely ground together in the molar ratio of 1.25:1:1, respectively. The mixture was heated in an alumina crucible at 850 °C for 24 h, re-ground, and then heated at 1050 °C for 24 h. The product was washed thoroughly with distilled water followed by acetone and oven-dried at 110 °C for 4 h. KCa₂Nb₃O₁₀ was also synthesized by direct reaction for comparison to the ion exchanged species. K₂CO₃ (Alfa Aesar, 99.997%), CaCO₃ (Alfa Aesar, 99.99%), and Nb₂O₅ (Alfa Aesar, 99.9985%) were ground together and pressed into 7 mm pellets by hand press (Sigma–Aldrich). The pellets were heated at 850 °C for 24 h and 1200 °C for two periods of 4 h with intermittent grinding and hand-press pelletization between each step.

RbCa₂Nb₃O₁₀ was used for ion-exchange with various mono-valent cationic species to prepare the series ACa₂Nb₃O₁₀ (A = H, NH₄, Li, Na, K, CuCl) as detailed in Table 1. For the ammonium and alkali-metal species, the parent was finely ground with the corresponding nitrate reagent (NH₄NO₃, Alfa Aesar, 99.999%; LiNO₃, Alfa Aesar, 99.99%; NaNO₃, Alfa Aesar, 99.999%; KNO₃, Alfa Aesar, 99.994%) and placed into an alumina crucible. The exchange reactions were carried out for 4 days in an ANO₃ molten salt with the ratio 1:10 for ammonium and lithium and 1:20 for sodium and potassium, at temperatures of 200 °C, 350 °C, 400 °C, and 400 °C, respectively. To synthesize (CuCl)Ca₂Nb₃O₁₀, RbCa₂Nb₃O₁₀ and anhydrous CuCl₂ (Alfa Aesar, 99.995%) were ground together in a Pyrex tube, hand-pressed into pellets, sealed under vacuum in a Pyrex tube and reacted at 325 °C for 10 days. Each of this series of products was washed and dried in the same fashion as the starting material. HCa₂Nb₃O₁₀ was formed by stirring RbCa₂Nb₃O₁₀ in 6 M HNO₃ (aq) at 60 °C for 4 days, with replenishment of the acid solution after 3 days. This product required isolation by centrifugation for the washing step because much of the solid was fine enough to permeate standard filter paper.

2.2. Characterization

Variable temperature X-ray powder diffraction (XRD) data were collected on a Philips X-Pert PW 3020 MPD diffractometer (Cu K_α radiation, λ = 1.5418 Å) equipped with a curved graphite monochromator and an Anton Paar HTK1600 variable temperature stage. To determine the structural evolution of the compounds with increasing temperature, XRD data were taken from 25 °C to 1000 °C under flowing nitrogen in 50 °C heating increments. Kinetically hindered transitions were studied with longer periods of heat treatment, ranging from 6 to 24 h. To isolate endothermic and exothermic events associated with phase changes, the materials were examined by differential scanning calorimetry (DSC) on a

Netzsch 404S thermal analysis system. Samples were heated and cooled in alumina or platinum pans at 10 °C/min to 1000 °C under flowing argon (50 mL/min). Thermogravimetric analysis (TGA) in tandem with DSC was used to monitor weight changes during decomposition on a TA Instruments SDT Q600 V8.3 system. Samples were characterized by scanning electron microscopy on a JEOL JSM-5410 SEM and electron dispersive spectroscopy (EDS) EDAX DX-PRIME microanalytical system to examine morphology and chemical composition at various stages of heating. The peak positions and lattice parameters were refined by a least-squares method with the programs ChekCell and FULLPROF [39, 40].

3. Results

RbCa₂Nb₃O₁₀ was indexed in the tetragonal system with space group *P4/mmm* (#123). The lattice parameters presented in Table 2 were refined using the method of least squares refinement and were found to be in good agreement with previous reports [35]. The lattice parameters of ACa₂Nb₃O₁₀ (A = H, NH₄, Li, Na, K, CuCl) were also consistent with literature values (Table 2), and EDS analysis showed minimal amounts of residual rubidium ion (Rb:Nb < 0.05:1.00).

Two of the species were found susceptible to hydration. At 25 °C, HCa₂Nb₃O₁₀·(H₂O)_n and β-NaCa₂Nb₃O₁₀·(H₂O)_n intercalate variable amounts of water inside the interlayer, increasing the magnitude of the c lattice parameter by up to 1.5 Å. The degree of hydration in air is strongly dependent on ambient humidity [23]. For HCa₂Nb₃O₁₀, endothermic dehydration is observed between 50 °C and 125 °C with a mass loss of 3.3% corresponding to ~1.9 waters of hydration. The event is correlated with the shifting of the [001] reflection to a higher angle and a dramatic drop in its intensity. Dehydration of the sodium species requires higher temperatures. A pronounced endothermic signal is observed centered on 150 °C, accompanied by a mass loss of 3.5% (~1.1 waters of hydration) and a significant [001] reflection shift. β-NaCa₂Nb₃O₁₀ continues to lose mass up to 400 °C, but above 225 °C the weight loss is minimal and is not accompanied by observable structural rearrangement. Each of the compounds ACa₂Nb₃O₁₀ (A = NH₄, Li, Na, K, CuCl) also demonstrate small degrees of hydration, measuring less than 1% of the total sample weight. The volatilizations, however, are unaccompanied by crystallographic changes, indicating that such processes likely represent loss of surface water.

ACa₂Nb₃O₁₀ when A = H, NH₄ are the least thermally stable of the family. In the decomposition, the interlayer cations are removed from the perovskite lattice via formation of a corresponding oxide. In a concerted step, HCa₂Nb₃O₁₀ evolves H₂O (1.6% mass loss observed, theoretically 1.73%) and (NH₄)Ca₂Nb₃O₁₀ evolves NH₃ and H₂O (4.7% observed, theoretically 4.85%). These transitions are correlated with an exothermic DSC signal centered at 315 °C for the hydrogen species, while the ammonium compound gives a sharper 350 °C exotherm followed by an endotherm at 365 °C. The residual salt in both cases is the poorly crystallized single phase Ca₄Nb₆O₁₉, previously described by Fang and coworkers [31]. Major reflections of this tetragonal byproduct appear in the XRD data at about 300 °C and 340 °C, respectively. Upon further heating to 570 °C, Ca₄Nb₆O₁₉ begins to disproportionate to CaNb₂O₆ (JCPDS File No. 39-1392) and Ca₂Nb₂O₇ (JCPDS File No. 42-2), accompanied by a DSC slope change in the exothermic direction.

Members of the series ACa₂Nb₃O₁₀ (A = Li, Na) are found to be more stable than the A = H and NH₄ species, yet with sufficient heating undergo rearrangement and decomposition. In neither case is mass loss observed after dehydration. In the XRD of LiCa₂Nb₃O₁₀, no change in crystal structure occurs up to 600 °C. At 680 °C DSC registers an endothermic event, correlated with a major shifting of reflections in the 650 °C and 700 °C diffractograms, representing the irreversible formation of an alternative polymorph of LiCa₂Nb₃O₁₀.

Table 1
Summary of ion-exchange reactions with RbCa₂Nb₃O₁₀ host.

Ion-exchanged product	Molar ratio	Temperature (°C)	Time (days)
HCa ₂ Nb ₃ O ₁₀ ·(H ₂ O) _n	Excess ^a	60	4
(NH ₄)Ca ₂ Nb ₃ O ₁₀	1:10 ^b	200	4
LiCa ₂ Nb ₃ O ₁₀	1:10 ^b	350	3
β-NaCa ₂ Nb ₃ O ₁₀ ·(H ₂ O) _n	1:20 ^b	400	7
KCa ₂ Nb ₃ O ₁₀	1:20 ^b	400	7
(CuCl)Ca ₂ Nb ₃ O ₁₀	1:2 ^c	325	10

^a 6 M HCl.

^b ANO₃ (A = NH₄, Li, Na, K).

^c Anhydrous CuCl₂.

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