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Multistep soft chemistry method for valence reduction in transition metal oxides with triangular (Cdl<sub>2</sub>-type) layers<sup>†</sup>

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Transition metal (M) oxides with MO<sub>2</sub> triangular layers demonstrate a variety of physical properties depending on the metal oxidation states. In the known compounds, metal oxidation states are limited to either 3+ or mixed-valent 3+/4+. A multistep soft chemistry synthetic route for novel phases with  $M^{2+/3+}O_2$  triangular layers is reported.

A large class of transition metal oxides with layered cation ordering and general formula AMO<sub>2</sub> (A = alkali metal, M = transition metal) are important from both fundamental and technological points of view due to the multitude of demonstrated physical properties (Fig. 1). α-NaFeO<sub>2</sub>, a prototype structure which lends its name to the structural type, crystallizes in a rocksalt-related lattice consisting of cubic close-packed oxygen layers with Fe<sup>3+</sup> and Na<sup>1+</sup> occupying the octahedral sites of alternating layers (Fig. 2). The presence of MO<sub>2</sub> triangular (CdI<sub>2</sub>-type) layers results in a large variety of physical properties, for example NaVO2 exhibits two successive orbital ordering transitions<sup>1</sup> and  $\alpha$ -NaFeO<sub>2</sub> has two antiferromagnetic structures.<sup>2</sup> AMO<sub>2</sub> phases are model compounds for geometrically frustrated magnets with NaTiO2 as a prominent example.3 In another report, it was found that NaTiO<sub>2</sub> has delocalized d electrons and a weak magnetic transition at 260 K.<sup>4</sup> Interestingly, broad fluctuating cross-over regimes were found in NaCrO<sub>2</sub>.<sup>5</sup> Below 45 K, NaMnO<sub>2</sub> has strongly coupled antiferromagnetic chains, resolving the geometric frustration present.<sup>6</sup> Adjusting the Na stoichiometry through low temperature Na deintercalation in Na<sub>r</sub>CoO<sub>2</sub> allowed for the determination of a physical properties vs. Co oxidation state phase diagram with a nonmagnetic insulator, spin-density wave (SDW), Curie-Weiss metal states and even superconductivity for a hydrated compound (Fig. 1).<sup>7-12</sup>

In spite of the high stability of the 2+ oxidation state for many transition metals, all layered  $A_xMO_2$  compounds contain transition metals in the 3+ or mixed valent 3+/4+ oxidation states. Even in layered Ag<sub>2</sub>NiO<sub>2</sub>, where the presence of Ag<sup>1+</sup> and Ni<sup>2+</sup> can be



Fig. 1 Schematic physical properties – Co oxidation state phase diagram for  $Na_xCoO_2$  cobaltates (based on ref. 8).

expected based on chemical intuition, XANES and XPS measurements confirm that subvalent silver [Ag2]<sup>1+</sup> units coexist with Ni<sup>3+</sup> ions.<sup>13,14</sup> As seen in Fig. 1, the  $M^{2+/3+}$  area for layered AMO<sub>2</sub> compounds is a large, empty space due to lack of materials with  $M^{2^{+/3^{+}}}O_2$  triangular layers. Expanding the available metal oxidation states in layered AMO<sub>2</sub> compounds to the 2+/3+ region will open up access to novel phases with unusual combinations of oxidation and spin states, leading to a large variety of physical properties. Investigation of the crystal and electronic structure-properties relationship for these compounds would advance our understanding of materials with strongly correlated electrons; however, the synthesis of such materials is a challenge which can not be addressed by traditional solid-state synthetic approaches. There is a fundamental crystallochemical reason why ArMO<sub>2</sub> compounds with M in the 2+/3+ oxidation state and layered A/M ordering are unstable. It has been previously noted that layered ordering is favoured by a large difference in the ionic radii R of  $A^{1+}$  and  $M^{3+}$ where an ionic radii ratio  $R_M/R_A < 0.86$  is typical for ordered phases.<sup>15</sup> It was calculated that the elastic energy associated with ions of different sizes stabilize M3+ and A1+ ordering into alternate layers.<sup>16</sup> Additionally, the smaller charge difference between M<sup>2+</sup> and A<sup>1+</sup> ions is unfavourable for ordering.

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 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: Full experimental details, PXD patterns of prepared phases, particle size information, SEM images, Li^{1+}/Na^{1+} intercalation rates, DSC curve, crystal structures description. See DOI: 10.1039/c3cc48836e



Fig. 2 The multistep soft chemistry procedure: (1) synthesis of NaMO<sub>2</sub> (M = 3d metal), (2) Na-ion deintercalation from the structure, (3) aliovalent Ca<sup>2+</sup> for Na<sup>1+</sup> exchange, and (4) Li<sup>1+</sup> or Na<sup>1+</sup> intercalation into the previously produced vacancies.  $MO_6$  octahedra are highlighted for clarity.

In this communication, a multistep low-temperature soft chemistry (chimie douce) approach for the synthesis of a family of compounds with MO<sub>2</sub> triangular layers and, uniquely, with transition metals in mixed valent 2+/3+ oxidation states is reported. While many oxides are traditionally synthesized by direct reactions at high temperatures, a soft chemistry approach allows for the preparation of new materials at lower temperatures in a predictable fashion. Topotactic reactions, where extensive parts of the original framework are retained, allow for greater control of the structure of the final product. Using a soft chemistry approach, we can choose a precursor phase and design a sequence of low-temperature reactions that will modify the structure in a stepwise fashion to yield a target product phase. The multistep procedure begins with the preparation of  $NaM^{3+}O_2$  (Fig. 2–Reaction 1), which requires substantially different condition for different metals. All NaMO<sub>2</sub>, unlike LiMO<sub>2</sub>, form wellordered layered structures; therefore, we selected Na containing compounds as starting phases. The second step is to adjust the Na content by a deintercalation reaction shown in Fig. 2-2 utilizing Br<sub>2</sub> or I<sub>2</sub> in MeCN as oxidation reagents. Co phases were used as a proof of principle. Na content in the initial  $Na_x M^{4-x}O_2$  phases eventually determines the transition metal oxidation state in the final compound synthesized after all 4 steps are complete. The second step is only viable for transition metals stable in the 3+/4+ oxidation states and should be skipped if an A<sub>0.5</sub>Ca<sub>0.5</sub>MO<sub>2</sub> final stoichiometry is desired. The third step, aliovalent ion exchange of  $Ca^{2+}$  for  $2Na^{1+}$  ions (Fig. 2–3), results in  $Ca_{x/2}M^{4-x}O_2$  phases with vacancies in the A position while preserving the metal oxidation state. The low eutectic temperature in the NaNO<sub>3</sub>-Ca(NO<sub>3</sub>)<sub>2</sub> system (214 °C) allowed for both an increased reaction speed above the eutectic temperature due to the presence of a melt as well as a low

reaction temperature, favourable for the formation of metastable phases and host structure retention. Low reaction temperature as well as the relatively large  $Ca^{2+}$  ionic radii are both important for this topotactic transformation.  $Ca_xCoO_2$  are known to be stable only below 450 °C.<sup>17</sup> It was also shown that the ion exchange of Na<sup>1+</sup> by the smaller Mg<sup>2+</sup> cation led to formation of a spinel structure.<sup>18</sup> The final step of this multistep procedure (Fig. 2–4) involves intercalation of alkali cations into the previously created vacancies, resulting in the reduction of the transition metal to the 2+/3+ oxidation state.

Complete  $Ca^{2+}$  for  $Na^{1+}$  exchange in  $Ca_xCoO_2$  was previously demonstrated;<sup>17</sup> therefore, despite using  $Na_xMO_2$  precursors, the final  $A_{1-x/2}Ca_{x/2}M^{3-4/x}O_2$  can contain any alkali elements. The proposed multistep chimic douce reaction sequence allows for the synthesis of compounds with *M* oxidation states between +2.5 and +3. Examples of  $Li^{1+}$  and  $Na^{1+}$  intercalation are presented herein. Compounds synthesized using this approach are presented in Table 1 with stoichiometries determined by quantitative inductively coupled plasma atomic emission spectroscopy. Microscopic homogeneity was confirmed by energy dispersive X-ray spectroscopy. The reactions corresponding to the synthesis of  $Li_{0.75}Ca_{0.25}$ .  $CoO_2$  are given below as an example of the procedure.

- $1/3Co_3O_4 + NaOH + 1/12O_2 \rightarrow NaCoO_2 + 0.5H_2O$  (1)
  - $NaCoO_2 + 0.25I_2 \rightarrow Na_{0.5}CoO_2 + 0.5NaI$ (2)

$$Na_{0.5}CoO_2 + 0.25Ca(NO_3)_2 \rightarrow Ca_{0.25}CoO_2 + 0.5NaNO_3$$
 (3)

 $Ca_{0.25}CoO_2 + 0.75n$ -BuLi  $\rightarrow Li_{0.75}Ca_{0.25}CoO_2 + 3/8C_8H_{18}$  (4)

As can be seen from the final compound stoichiometries (Table 1), it was not always possible to fill vacancies completely

Table 1 Stoichiometries, space groups and unit cell parameters of the prepared compounds

Compound	Space group	Cell parameters (Å, $\beta$ in $^{\circ}$ )	M Ox. state
$Li_{0.49(1)}Ca_{0.50(1)}Fe_{1.00(1)}O_2$	C2/m	a = 5.173(4), b = 5.948(2)	+2.51
$Na_{0.50(2)}Ca_{0.50(1)}Fe_{1.00(1)}O_2$	C2/m	$c = 5.804(1), \beta = 73.12(4)$ a = 5.179(6), b = 5.964(3)	+2.50
	$C_{2}/m$	$c = 5.802(1), \beta = 73.24(1)$ a = 4.789(2), b = 4.027(5)	+2.52
$LI_{0.47(1)}Ca_{0.50(1)}CO_{1.00(1)}O_{2}$	C2/m	a = 4.789(3), b = 4.027(3) $c = 5.696(3), \beta = 107.5(2)$	+2.33
$Na_{0.31(2)}Ca_{0.50(1)}Co_{1.00(2)}O_2$	$R\bar{3}m$	a = 2.831(1), c = 16.288(3)	+2.69
$Li_{0.64(2)}Ca_{0.37(2)}Co_{1.00(1)}O_2$	$P6_3/mmc$	a = 2.818(2), c = 10.820(6)	+2.62
$Na_{0.59(1)}Ca_{0.37(1)}Co_{1.00(1)}O_2$	$P6_3/mmc$	a = 2.856(2), c = 10.809(3)	+2.67
$Li_{0.75(1)}Ca_{0.25(1)}Co_{1.00(1)}O_2$	$P6_3/mmc$	a = 2.817(4), c = 10.794(5)	+2.75
$Na_{0.67(2)}Ca_{0.25(1)}Co_{1.00(1)}O_{2}$	$P6_3/mmc$	a = 2.828(6), c = 10.851(2)	+2.83

with  $Li^{1+}$  or  $Na^{1+}$  during the 4th step of the procedure, especially in the case of larger  $Na^{1+}$  ions. Nevertheless, all the prepared compounds are highly crystalline, shown by narrow peaks in powder X-ray diffraction patterns (Fig. 3). Peak broadening in the PXD pattern of  $Na_{0.59}Ca_{0.37}COO_2$  is related to a smaller particle thickness determined by the Whole Powder Pattern Modeling (WPPM) algorithm (Table S1, ESI<sup>†</sup>).<sup>19</sup> The particle thickness decreased systematically with each soft chemistry reaction.

The multistep chimie douce reaction sequence outlined above can be described as an "aliovalent exchange plus intercalation" procedure. A thorough literature search revealed that a similar approach was demonstrated once for a Ruddlesden–Popper phase but has never been utilized for any other structural types.<sup>20,21</sup>

Emphasis needs to be placed on that fact that both the intermediate and final compounds are metastable and can not be directly prepared – a unique aspect of the described multistep chimie douce procedure. Decomposition of the final compounds occurs at relatively low temperatures (110 –250 °C) in both O<sub>2</sub> as well as N<sub>2</sub> atmospheres according to thermal gravimetric analysis (TGA) data.

It is important to note the role of Ca<sup>2+</sup> as "pillars" between the MO<sub>2</sub> layers, effectively stabilizing the structures with M<sup>2+</sup> ions. For example, since the ionic radii of Ca<sup>2+</sup> in an octahedral environment (1.14 Å) is much larger than that of Fe<sup>2+</sup> (high spin (HS) -0.92 Å),<sup>22</sup> the radii ratio  $R(Fe^{2+}/Ca^{2+}) = 0.81$ , well below the empirical 0.86 value needed for layered ordering.<sup>15</sup> Since the Fe<sup>2+</sup> radii is similar to that of Li<sup>1+</sup> (0.90 Å), the



Fig. 3 Powder X-ray diffraction patterns for  $Na_{0.74}CoO_2$ ,  $Ca_{0.37}CoO_2$  and  $Na_{0.59}Ca_{0.37}CoO_2$ .

direct synthesis of layered compounds without Ca<sup>2+</sup> pillars is impossible.

Predicting the physical properties of novel  $A_{1-x/2}Ca_{x/2}MO_2$ phases is difficult; nevertheless, by considering the expected structures and electronic states, some conclusions can be drawn. For example, in thermoelectric cobaltates, the Seebeck coefficient is related to the entropy transport associated with the different number of electronic microscopic states g.<sup>23</sup> Using the Koshibae formula for  $Na_{0.5}CoO_2$  (g(Co<sup>4+</sup>-low spin (LS)) = 6;  $g(\text{Co}^{3+}\text{-LS}) = 1$ ), a large Seebeck coefficient value – 154  $\mu$ V K<sup>-1</sup> – is obtained. Among all possible oxidation states and spin combinations for any 3d transition metal, A<sub>0.5</sub>Ca<sub>0.5</sub>CoO<sub>2</sub> with  $Co^{2+}$  in the HS state (g = 12) and LS  $Co^{3+}$  can be expected to have the largest Seebeck value at  $-214 \text{ }\mu\text{V}\text{ }\text{K}^{-1}$  – even higher than reported in  $Co^{3+/4+}$  cobaltates. Due to the spin blockade phenomenon - a mechanism suggested to explain the low electronic conductivity in materials with Co2+-HS and Co3+-LS -Na<sub>0.31</sub>Ca<sub>0.5</sub>CoO<sub>2</sub> will probably have low electronic conductivity as well.24

When  $Li^{1+}$  ions are intercalated into the vacancies produced during aliovalent exchange, the products are potential Li-ion cathode materials.  $Li_{0.49}Ca_{0.5}FeO_2$  is the first known  $Fe^{2+}/Fe^{3+}$ layered lithium iron oxide. According to preliminary results,  $Li^{1+}$  can be cycled to a degree in this material without optimization.

In conclusion, a facile multistep synthetic method for producing novel compounds with  $M^{2+/3+}O_2$  triangular (CdI<sub>2</sub>-type) layers is presented. A variety of possible magnetic, thermoelectric, and electrochemical properties exhibited in this new family of layered phases with reduced oxidation states warrants further investigations. Such studies as well as the synthesis of family members with other transition metals are currently underway and will be published separately.

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