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A New Approach to Synthesis of Layered Fluorites Containing Molecular Anions: Synthesis of $Ln_2O_2CO_3$, $K(LnO)CO_3$, and $Ln_2O_2CrO_4$ via Metathesis Reactions

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A new synthetic approach is suggested for preparation of layered rare-earth oxide compounds containing $[Ln_2O_2]$ slices and molecular anion sheets (CO_3^{2-}, SO_4^{2-}, and CrO_4^{2-}). It is based on exchange reactions of rare-earth oxychlorides, $[Ln_2O_2]Cl_2$, and alkali carbonates, sulfates, or chromates. Five new rare-earth oxychromates $[Ln_2O_2]CrO_4$ (Ln = Pr−Gd) have been prepared which adopt a new, probably layered, structure type. In addition, significantly easier and more efficient synthetic pathways were found to the known compounds $[Ln_2O_2]K_2(CO_3)_2$ and $[La_2O_2]CrO_4$. The structure of the latter compound has been determined from neutron powder diffraction data. Factors affecting reaction pathways and products are discussed, as well as prospects for applying the approach to more complex layered compounds.

Introduction

For the recent several decades, extensive investigations have focused on compounds with layered (2D) structures, in particular on 2D fluorite and perovskite derivatives. The interest in these compounds initiated from various important properties exhibited by many of their representatives, e.g., superconductivity,[1] ferroelectricity,[2] ionic conductivity,[3] and exchange, including trapping of toxic[4] and radioactive[5] anions, etc. Another source of interest stems from their particularly versatile crystal chemistry involving, e.g., complicated mixed-layer structures with stacking periods of up to 90 Å,[6] stabilization of unusual coordination polyhedra, and even nonambient or new polymorphic forms as 2D fragments.[7] Besides, the 2D character of structure has a strong effect on their reactivity, invoking reactions not possible among compounds of other dimensionality. For instance, when robust slabs, tightly "armed" with covalent intralayer bonds, interleave with sheets of monatomic or small molecular ions attached only by electrostatic (noncovalent) forces, the latter may undergo various exchange reactions while the former are left intact and act as 2D infinite fundamental building units. In the simplest cases, the structural motif remains in general (Figure 1a); such reactions are suggested to immobilize radioactive halide ($^{36}Cl^-$, $^{131}I^-$) or toxic selenite anions. A more complex variant is an assembly of two layers from different precursors. The dimensionality of the resulting structure may vary from 2 (Figure 1b) to 3 (Figure 1c) with a 2D ordering or superstructure, e.g., of perovskites.[8,9] The side products, commonly halides or nitrates, are easily removed by dissolution.

The advantages of the metathetic synthesis pathways have been understood just recently, but their development has

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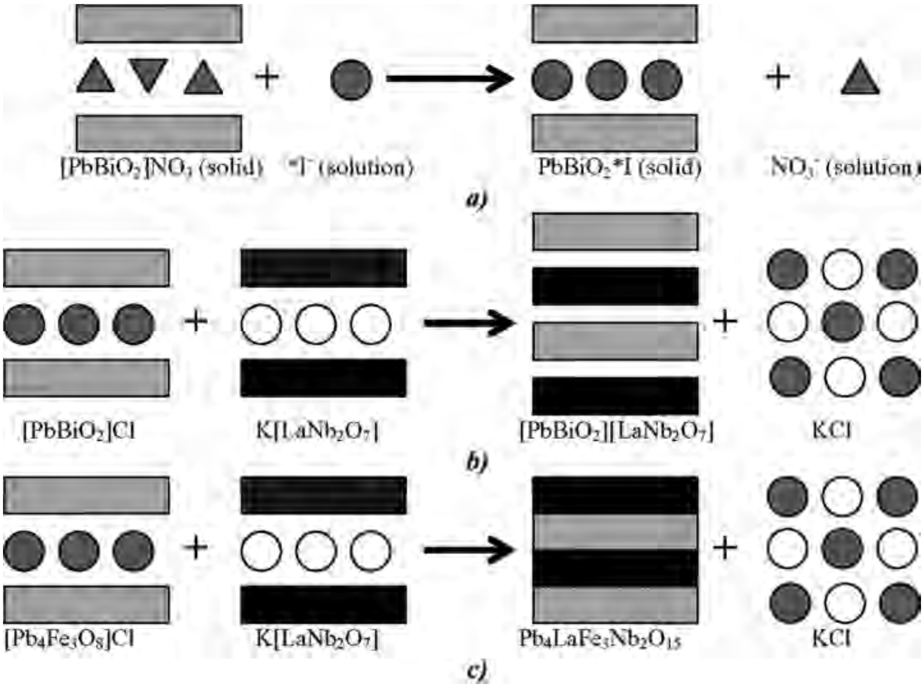

Figure 1. Schematic representation of various kinds of metathesis products: (a) anion exchange, the cationic layer, and hence the structure motif, remains almost intact;[4] (b) layer exchange, the layered character of structure survives,[10] as well as integrity of the assembling layers; (c) formation of 2D ordered perovskite by coalescence of an "oxygen-deficient" (positively charged) and an "oxygen-precise" (negatively charged) perovskitic layers. A model reaction, not yet studied, is suggested.

already permitted to essentially soften synthesis conditions and provide more efficient and, in the most interesting cases, unique approaches to many otherwise inaccessible metastable compounds.[10–12] The reference data being too scattered, the key factors which determine the nature of the reaction pathways and products (hence the choice of appropriate precursors and synthesis conditions) cannot be formulated as yet. Nevertheless, one can conclude that geometrical factors play a significant role, particularly the size of not only exchanged ions but also those contributing to the assembling layers. For instance, reactions of isostructural $Ca_2CuO_2Cl_2$ and $Sr_2CuO_2Cl_2$ with $NaLaTiO_4$ lead to different products.[13] A similar sensitivity to the nature of precursors is observed upon interaction of $KLaNb_2O_7$ with $FeCl_2$ and $FeBr_2$, where $FeClLaNb_2O_7$ and $Fe_{0.5}LaNb_2O_7$ are formed, respectively.[14,15] Evidently, systematic studies of model systems are necessary to reveal the general trends in the realm of these unusual reactions.

In most cases addressed so far, the exchanged negatively charged part of the structures consisted of single or double halide or nitrate sheets. The simplest structures bearing these elements are those of Sillén-type oxyhalides and oxynitrates,[5,10,16,17] e.g., $[BiPbO_2]NO_3$ or $[Ln_2O_2]Cl_2$ can serve as simple models for more complex perovskite oxyhalides like $[Pb_4Fe_3O_8]Br$[18] or $[Sr_4Co_2O_6]Cl_2$.[19] The same $[Ln_2O_2]$ moieties as in $[Ln_2O_2]Cl_2$ are suggested to exist in the structures of $[Ln_2O_2]CO_3$ (T-forms,[20] Figure 2a) and $[La_2O_2]CrO_4$,[21] and found in the structures of $[Ln_2O_2]$-

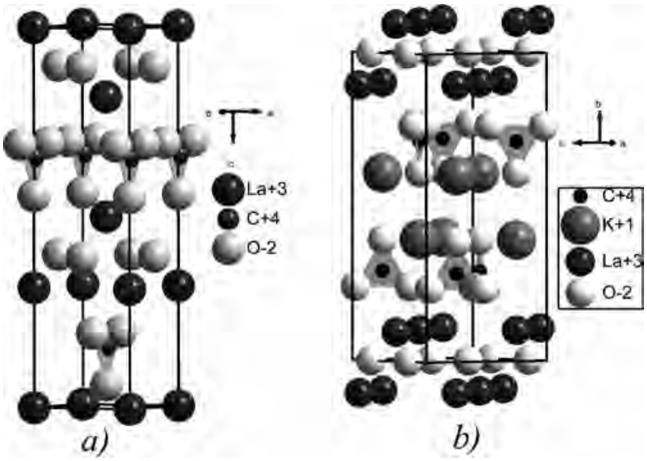

Figure 2. Structures of (a) T-$[Ln_2O_2]CO_3$ (proposed) and (b) $[Ln_2O_2]K_2(CO_3)_2$.

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SO_4,[22,23] $[Ln_2O_2]K_2(CO_3)_2$[24] (Figure 2b), etc. Preparation of some of these compounds via traditional approaches faces sufficient difficulties. The T-forms of $[Ln_2O_2]CO_3$ are obtained upon thermal decomposition of $Ln_2(CO_3)_3 \cdot xH_2O$ as poorly crystallized intermediates which, upon further heating, irreversibly convert into thermodynamically stable pseudohexagonal monoclinic (H-)forms. Due to low crystallinity, characterization of the T-forms is incomplete. Preparation of $[La_2O_2]CrO_4$ via a traditional ceramic route (from La_2O_3 and Cr_2O_3) requires high temperatures and oxygen pressure. At ambient conditions, $[La_2O_2]CrO_4$ is evidently metastable relative to $LaCrO_3$, La_2O_3, and O_2.[25] Preparation of $[Ln_2O_2]K_2(CO_3)_2$ involves a rather complex process of slowly oxidizing HCOOK melts containing several wt % of Ln_2O_3 which is limited to 1−2 g of target products; in addition, formation of a $Ln(OH)_3$ admixture seems to be inevitable.[24] No Ce^{III}-based analogues could be prepared as yet, since wherever oxidizing media are involved (e.g., the presence of reducible anions or air at high temperatures) oxidation into stable CeO_2 is favored.

From our point of view, the exchange reaction pathways starting from easily accessible $[Ln_2O_2]Cl_2$ and appropriate alkali salts of the molecular dianions, i.e., carbonates, sulfates, etc., seem to be promising. An expected advantage is that external aggressive media are not necessary and can be dispensed, as the reactions can be conducted in isolated space.

In the current paper, we report the first results of our studies of reactions between rare-earth oxychlorides and alkali salts of selected molecular anions (CO_3^{2-}, SO_4^{2-}, SeO_4^{2-}, CrO_4^{2-}, MoO_4^{2-}, and WO_4^{2-}). In addition, the reactivity of several compounds isostructural to LnOCl was tested.

Experimental Section

The starting compounds were rare-earth oxychlorides and corresponding anhydrous alkali salts which were mixed in appropriate ratios, thoroughly ground, and placed into silica-jacketed alumina crucibles. The silica tubes were evacuated to the residual pressure of 0.1−0.05 Torr, torch-sealed, and annealed in a programmable furnace under varied regimes. The products were washed several times with copious amounts of distilled water and dried in air. The isostructural compounds tested as possible analogues of LnOCl were BiOCl, BaFCl, and PbFCl.

The LnOCl precursors were synthesized via pyrohydrolysis of $LnCl_3 \cdot 6H_2O$. Usually, a sample was heated in a wet air stream at 550 °C for 2–3 h and cooled in dried air as the resulting oxychlorides slowly absorb water at low temperatures.[26] In the case of Ce, Pr, and Tb, hydrogen was used instead of air, to prevent oxidation to Ln^{IV}. The LnOCl (Ln = La−Dy) precursors were obtained phase-pure except CeOCl where some batches contained ca. 1% of CeO_2 which is inert toward exchange reactions.

BaFCl was obtained by annealing BaF_2 and $BaCl_2$ at 750 °C for 48 h in a silica-jacketed alumina crucible.[27] PbFCl was obtained by coprecipitation of PbF_2 and $PbCl_2$ by slow dropwise addition of lead nitrate solution to a hot (60–70 °C) solution containing a 1.05:1 mixture of NaF and NaCl under vigorous stirring. BiOCl was used as purchased.

Li_2CrO_4 was obtained by adding Li_2CO_3 to a hot aqueous solution of CrO_3. The yellow solution was evaporated and yellowish orange product recrystallized several times. K_2MoO_4 and K_2WO_4 were obtained by annealing K_2CO_3 and MoO_3/WO_3 at 700 °C overnight. Alkali carbonates A_2CO_3 (A = Li−Cs), Na_2CrO_4, K_2CrO_4, K_2SO_4, and K_2SeO_4 (purity >99.5%) were used as purchased. All alkali precursors were dried at 300 °C for 1−2 h prior to the reactions.

X-ray characterization of the precursors and resulting products was made using a Guinier camera (FR-552, Enraf-Nonius) with semiconductor quality germanium as an internal standard. Chemical composition was determined via energy dispersive X-ray (EDX) analysis on a JEOL JEM 2011 HRTEM microscope with an Oxford Instruments ISIS EDX Analysis System.

The powder neutron diffraction data were collected on the high-flux powder diffractometer D2b at the ILL, Grenoble. The La_2CrO_6 sample was loaded into a vanadium can, and data were collected at 25 °C for about 2 h, at a wavelength of 1.5943 Å. Rietveld data analysis was carried out using the GSAS program suite.[28]

Results

Carbonates. Reactions of LnOCl (Ln = La, Sm) with A_2CO_3 (A = Li−Cs) proceed completely at 500−550 °C within 48−55 h. The insoluble residues, except for A = K, are phase-pure H-forms of $[Ln_2O_2]CO_3$. The X-ray patterns contain sharp and clearly resolved reflections. When A = K, the corresponding $[La_2O_2]K_2(CO_3)_2$ complex carbonate is formed at 550 °C from 2LaOCl−3K_2CO_3 mixtures. Lowering the annealing temperature results in increasing amounts of H−$La_2O_2CO_3$ which is the sole product when 2LaOCl−K_2CO_3 mixtures are heated.

With Ln = Ce, no layered oxycarbonate had been obtained. After annealing, the capsules opened with a clap indicating internal pressure. The X-ray pattern of a black product indicated presence of CeO_2 as the only cerium-containing product.

Sulfates and Selenates. The $[Ln_2O_2]SO_4$ compounds are structurally well-characterized, and their synthesis conditions are relatively simple.[29] Thus, only LaOCl and CeOCl were studied as reference and target systems. Reaction of LaOCl and K_2SO_4 is complete after a 48 h annealing at 750 °C producing a well-crystalline $La_2O_2SO_4$ product. However, CeOCl reduces K_2SO_4 to SO_2 and elemental sulfur, akin to the carbonate case. Our attempts to prepare $[La_2O_2]SeO_4$ from LaOCl and K_2SeO_4 at the same or milder conditions yielded only La_2SeO_5 (JCPDS File # 51-1803). When BiOCl was used instead of LaOCl, a related Bi_2SeO_5 compound[30] was observed along with traces of unknown by-phases.

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Table 1. Optimized Synthesis Conditions and Monoclinic Cell Parameters for the Ln_2CrO_6 Compounds (Ln = La, Pr−Gd)

compound	synthesis conditions	structure type	cell parameters			
			a, Å	*b*, Å	*c*, Å	*β*, deg
La_2CrO_6	750 °C, 48 h	$Pb_2F_2SO_4$	14.396(3)	4.4052(8)	8.467(2)	107.36(2)
Pr_2CrO_6	600 °C, 48 h		15.576(5)	8.015(2)	4.065(1)	92.03(2)
Nd_2CrO_6			15.640(4)	8.074(1)	4.080(1)	92.11(1)
Sm_2CrO_6	600 °C, 55 h	new	15.474(3)	7.925(2)	4.028(1)	92.02(2)
Eu_2CrO_6	575 °C, 55 h		15.472(4)	7.876(4)	4.012(1)	92.23(3)
Gd_2CrO_6			15.723(6)	7.761(2)	4.001(1)	92.90(2)

Chromates. Reactions between rare-earth oxychlorides and alkali chromates were studied in most detail. Due to the deep color of chromium compounds, the reactions could be monitored macroscopically. The sample was considered fit for further investigations if there was no yellow coloring of rinsewater and no green Cr^{III}-containing products were present in the insoluble residue. Upon reaction of LaOCl with Li_2CrO_4, reduction to Cr^{III} starts above 300−350 °C, even before the exchange reaction is complete. With Na_2CrO_4, the exchange completes at 520−550 °C, but the low-quality X-ray diffraction (XRD) of the yellow product shows nothing common with that of La_2CrO_6 (JCPDS File #26-0817). At higher temperatures, green decomposition products appear. The best result was obtained when $2LaOCl-K_2CrO_4$ mixtures were annealed at 700−750 °C for 48 h. The XRD pattern of La_2CrO_6 product is of excellent quality and shows well-resolved splitting of some strong lines into very narrow doublets which indicates a monoclinic superstructure similar to $[Ln_2O_2]SO_4$. The exchange reaction between LaOCl and K_2CrO_4 may also proceed in open alumina crucibles, but the X-ray reflections are sufficiently broader and the doublets are not resolved. The method is fit for large-scale synthesis (amounts as large as 10 g can be prepared in one batch). It should be noted that complete reduction of chromium was observed each time when a $LnOCl-K_2CrO_4$ sample was heated in contact with silica (e.g., when traces of the reaction mixture fell onto the bottom of silica jacket upon filling the alumina crucible or were thrown out by air stream upon evacuation).

For other Ln, only reactions with K_2CrO_4 were studied. For Ln = Ce, the gray product was a fine mixture of CeO_2 and Cr_2O_3. In the case of Pr and Tb, the reaction products were of colors resembling those of intermediate oxides, Pr_6O_{11} and Tb_4O_7. However, X-ray patterns of products with Pr−Gd are very similar, indicating a new family of isostructural compounds, however different from La_2CrO_6. EDX of the Nd sample confirmed expected "Nd_2Cr" composition (no residual K or Cl were detected). The XRD pattern of Pr_2CrO_6 was indexed using the TREOR90[31] program with monoclinic unit cell parameters and cell volume only slightly larger than that of La_2CrO_6. When passing from Pr to Dy, the maximal synthesis temperature decreases from 700 to 500 °C which results in lowering of crystallinity degree and quality of X-ray pattern. In addition, a new set of lines is observed starting from Eu, its intensities increasing with Ln number. For the Tb sample, only several weak lines suggest the presence of a Nd_2CrO_6-type compound which disappear from Ln = Dy, where only a new set of lines is present on the X-ray diagrams. For the X-ray pattern of the Dy sample, certain similarities can be followed with the (unindexed) pattern of Bi_2CrO_6 (JCPDS File #01-0738); however, the low quality of the powder diagram did not permit us to accurately determine and index the reflections. Investigations of systems with late rare-earth systems are underway and will be reported in a separate contribution. Optimal synthesis conditions and cell parameters for the La−Gd compounds are summarized in Table 1. For Tb_2CrO_6, the cell parameters could not be calculated due to a small number and broadness of lines.

An attempt was made to grow single crystals of La_2CrO_6 from a CsCl flux. A LaOCl:CsCl = 1:10 sample was annealed at 700 °C for 1 day followed by slow cooling. No crystals appeared, and a reverse reaction (toward LaOCl and Cs_2CrO_4) was found to partially proceed.

The reaction of BiOCl and K_2CrO_4 was studied between 475 and 625 °C where the (reversible) exchange process is almost complete and most BiOCl is consumed. The peaks given in the JCPDS File # 01-0738 were present on X-ray diagrams, but their number is much larger. The X-ray patterns could not be indexed which suggests that more than one phase is in fact produced. Further studies are currently underway, and a complete report will be given elsewhere.

Reactions of PbFCl and BaFCl with K_2CrO_4 were studied between 250 and 300 °C and 550 and 600 °C, respectively. In both cases, amorphous intermediates are formed first which at higher temperatures convert into mixtures of MF_2 and $MCrO_4$ (M = Pb, Ba) as the sole crystalline products.

Trial reactions of LnOCl (Ln = La, Pr, Nd) and $K_2Cr_2O_7$ (2:1) at 550 °C/48 h led to stable $KLn(CrO_4)_2$ (PDF # 44-1179, 45-0199, and 45-0200) as the main crystalline products.

Molybdates and Tungstates. Reactions of LaOCl and K_2MoO_4/K_2WO_4 did not yield the desired Ln_2MO_6 oxides. In the tungsten case, $La_3WO_6Cl_3$ was identified as a main product. According to the very similar X-ray patterns of insoluble residues, $La_3MoO_6Cl_3$ is isostructural to $La_3WO_6Cl_3$.[32] No further investigations were made.

Structure Determination

Berjoan et al.[21] suggested an orthorhombic unit cell for $[La_2O_2]CrO_4$ by analogy with the $[Ln_2O_2]SO_4$ oxysulfates. A similar unit cell had also been proposed for a structural analogue, $[Pb_2F_2]SO_4$. However, as Kampf[33] pointed out, the true monoclinic cell is twice as large as the orthorhombic

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Table 2. Experimental Data for La_2CrO_6

formula weight	425.8
color	dark yellow
structure type	$Pb_2F_2SO_4$[32]
crystal system	monoclinic
space group	*C*2/*c* (No. 15)
cell parameters (errors):	
a, Å	14.4001(2)
b, Å	4.4095(1)
c, Å	8.4719(1)
β, deg	107.362(1)
V, Å^3	513.43(2)
Z	4
calculated density	5.509(1)
analyzing package	GSAS[28]
radiation and wavelength	neutrons, $\lambda = 1.5943$ Å
2θ range (deg)	5−160
number of free parameters	49
number of data points	3098
number of reflections	520
R_p, R_{wp}	0.0563, 0.0436
R_p, R_{wp} (excluding background)	0.0467, 0.0393
$R(F^2)$	0.0515
χ^2	0.19

subcell. The same applies also to $[Ln_2O_2]SO_4$.[22,23] Our good quality XRD pattern of $[La_2O_2]CrO_4$ indicated that its true cell is also monoclinic. Since no single crystals could be produced, a ~7 g sample was prepared using the above-described technique and neutron diffraction was applied to structure determination.

The refinement started from atomic coordinates of $[La_2O_2]SO_4$[22] and proceeded smoothly to yield low *R* values and high accuracy of atomic and structural parameters (Tables 2−4). Bond valence sums were calculated using the program VaList.[34] Final Rietveld refinement plot for $[La_2O_2]CrO_4$ is given in Figure 3. The crystal structure is shown in Figure 4. Anisotropic refinement of the O2 and O3 atoms constituting the CrO_4 tetrahedron did not reveal any tendency to disorder or distribution over different orientations.

Discussion

Successful synthesis of several new compounds and significant simplification of synthesis conditions for some known ones demonstrate that exchange reactions can be a useful and efficient synthetic tool in the areas where the traditional approaches fail or require hard conditions. Considering both our and reference data, several factors affecting the pathways and products of exchange reactions can be collected into "geometrical" and "chemical" groups.

Geometrical Factors. As we have pointed out in the Introduction, there are two types of geometrical parameters, i.e., the size of both exchanged ions and ions constituting the "intact" parts of the target structure. The reactions leading to metastable Ln_2CrO_6 compounds are particularly sensitive to the nature of exchanged alkali metal of the alkali chromates, so they provide a clear illustration. In general, one is tempted to suggest that the lowest synthesis temperature would be achieved when small alkali cations with highest mobility, e.g., Li^+, are employed, and use of large cations like Cs^+ would retard the exchange process and require higher temperatures. However, there are competitive factors, the polarizing ability of the exchanged cation, which is highest for Li^+, and melt formation which seems to be detrimental for Ln_2CrO_6; the melting point of the eutectic between resulting LiCl and unreacted Li_2CrO_4 is expected to be quite low. The use of potassium chromate as a precursor for Ln_2CrO_6 synthesis is thus a compromise. For heavier alkali cations, higher temperatures would be necessary which are expected to exceed the melting points of the corresponding chlorides invoking the liquid phase once again. Our results on a La_2CrO_6−CsCl mixture show that a reverse reaction starts in the melt, and a metastable (not involving more stable $LaCrO_3$) equilibrium is likely to be reached.

The second geometrical parameter is the relationship between size parameters of assembling layers. It determines whether an exchange, not decomposition, reaction would proceed. In the resulting structure, the geometrical parameters of all layers are assumed to be equal in the directions normal to stacking axis. Such an adjustment of the layer geometry in general is possible only via deformations of polyhedra constituting the layers. These deformations can stretch to certain degrees only, setting the stability limits for proposed structure types. Two relatively rigid layers can assemble in one structure only if the ratio of their dimensions is close to unity. This is the most likely reason for nonoccurrence of a complex perovskite upon reaction of $Sr_2CuO_2Cl_2$ with $NaLaTiO_4$ since size disagreement between various parts of the suggested $Sr_2La_2CuTi_2O_{10}$ structure is too large and exceeds its stability limit.

In the Ln_2CrO_6 compounds, the geometrical criterion of stability is reflected in the change of structure when passing from La to its successors. The $[La_2O_2]$ layers in the $[La_2O_2]CrO_4$ structure are severely stretched (cf. *d*(La−O) = 2.38 Å and α(LaOLa) = 104.7° × 4 and 119.4° × 2 in the $[La_2O_2]Cl_2$ precursor[35]) to accommodate the much more rigid CrO_4^{2-} anions which appear almost regular (Table 4). The difficulties of packing the CrO_4^{2-} anions between $[Ln_2O_2]^{2+}$ slabs within the $La_2O_2SO_4$ type are reflected by slight underbonding of the chromate oxygens (Table 3). The compound corresponds to the stability limit of the $[Pb_2F_2]SO_4$ structure type, and a different atomic arrangement appears for compounds of Pr−Tb. A preliminary X-ray structural study of Nd_2CrO_6[36] has confirmed presence of the distorted $[Nd_2O_2]$ fluorite slabs in the structure with the Cr atoms located between the slabs as expected; however, due to heavy absorption of conventional Cu*K* radiation by both Cr and Nd, a detailed structure and orientation of the CrO_4 groups could not be established. The complete structure of Nd_2CrO_6 is planned to be a topic of a separate communication. The stability limit of this structure is in turn exhausted at Ln = Tb.

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(36) Preliminary crystallographic data for Nd_2CrO_6: monoclinic, $P2_1/m$, $a = 15.616(1)$ Å, $b = 8.0239(6)$ Å, $c = 4.0672(3)$ Å, $\beta = 92.142(5)°$, $R_p = 0.076$.

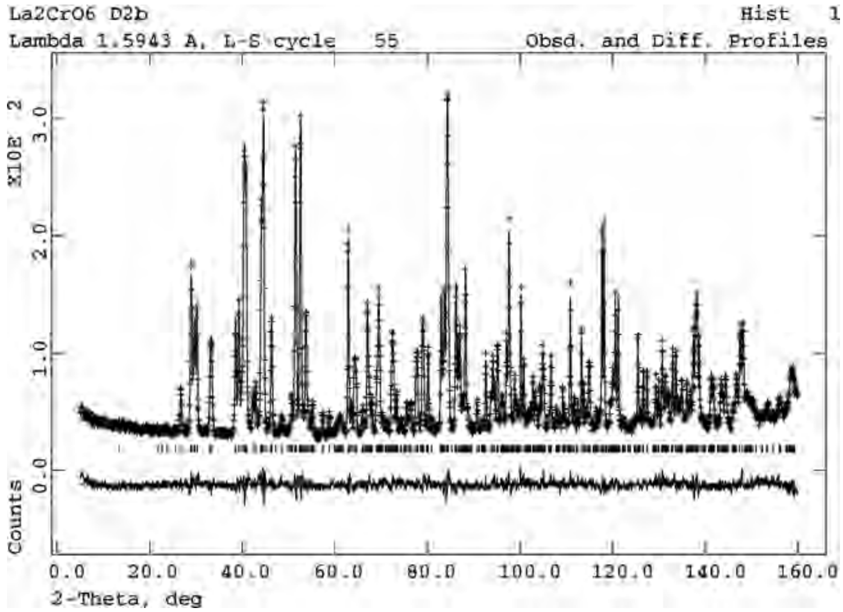

Figure 3. Final Rietveld refinement plot for $[La_2O_2]CrO_4$ (PND data).

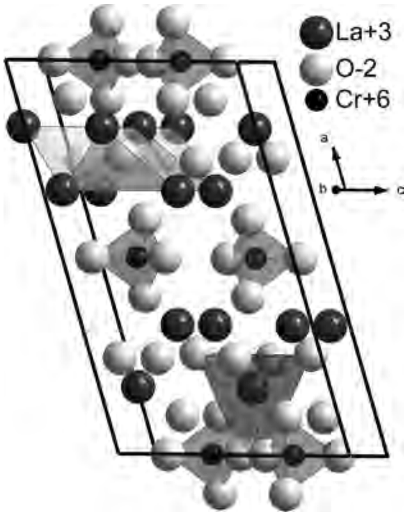

Figure 4. Crystal structure of $[La_2O_2]CrO_4$. The anisotropically refined O atoms constitute the CrO_4 tetrahedron.

Table 3

Atomic Positions for La_2CrO_6

atom	x	y	z	$U_{iso}/U_{equiv} \times 100$	BVS
La	0.17022(9)	0.4935(4)	0.0853(2)	0.37(2)	2.94
Cr	0	0.0426(9)	0.25	0.74(9)	6.00
O1	0.2437(1)	−0.0176(5)	0.1220(2)	0.50(3)	2.02
O2	−0.0009(2)	0.2671(4)	0.0917(2)	1.15	1.94
O3	0.0982(1)	−0.1641(5)	0.2979(3)	1.48	1.97

Anisotropic Thermal Parameters × 100.0

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O2	1.6(1)	0.8(1)	1.2(1)	−0.1(1)	0.6(1)	0.5(1)
O3	1.6(1	1.9(1)	1.2(1)	1.1(8)	0.6(1)	0.5(1)

Table 4. Bond Distances and Angles for La_2CrO_6

bond	distance	bond valence	angle	value
La−O1	2.470(3)	0.45	La−O1−La	130.77(8)
	2.380(3)	0.57		102.94(9)
	2.420(2)	0.51		104.33(9)
	2.436(2)	0.49		100.35(9)
La−O2	2.674(3)	0.26		99.25(9)
	2.670(3)	0.26		121.51(8)
La−O3	2.777(3)	0.20	O2−Cr−O2	107.0(3)
	2.758(8)	0.21	O2−Cr−O3	109.3(1) × 2
Cr−O2	1.664(3) × 2	1.20 × 2		109.6(1) × 2
Cr−O3	1.629(3) × 2	1.31 × 2	O3−Cr−O3	111.9(3)

A similar geometrical criterion applies to layered oxycarbonates where only potassium contributes to the complex $[Ln_2O_2]K_2(CO_3)_2$ structure (Figure 2b). In fact, the K−O bonds within the $K-CO_3$ layers are almost parallel to (001) planes and suggest a [100] cell parameter of ca. 3.9 Å, while OLn_4 tetrahedra of the $[Ln_2O_2]$ fluorite slabs dictate very close values of 3.95−3.85 Å. Neither smaller Na^+ nor larger Rb^+ can be accommodated since the size of $[A_2(CO_3)_2^{2-}]$ slabs would differ too much from that of $[Ln_2O_2]^{2+}$. The Ln^{3+} smaller than Eu^{3+} are also not tolerated since now the fluorite slices are too small to be combined with $[K_2(CO_3)_2^{2-}]$. Our results are in complete agreement with reference data,[24] though different synthetic procedures have been utilized.

Chemical Factors. The chemical factors "forbidding" exchange pathways are redox and secondary reactions. Redox reactions are the most frequent restrictions which are well demonstrated by reactions of CeOCl and K_2CO_3 or K_2CrO_4. In the solid state, CeO_2 is the most stable compound and redox reactions proceed instead of exchange at quite low temperatures. Since Ce^{IV} is a one-electron reductant, one could expect that CO_3^{2-} would be converted to CO: "$Ce_2O_2CO_3$" → $2CeO_2 + CO$. However, appearance of a black amorphous substance suggests further disproportionation and partial reduction of CO_3^{2-} to elemental carbon: $4CeOCl + 2K_2CO_3 \rightarrow 4CeO_2 + 4KCl + C + CO_2$. A related, but more complex process, takes place upon reaction of CeOCl and K_2SO_4. Note that redox reactions also proceed upon synthesis of Pr_2CrO_6 and Tb_2CrO_6, but the amount of Ln^{IV} is expected to be small since all compounds are isostructural and dependence of cell volume vs Ln^{3+} radius is relatively smooth. Since Pr^{IV} is more stable than Tb^{IV}, the deviation for Pr_2CrO_6 is more evident than that for Tb_2CrO_6.

Comparison of structural parameters for $[La_2O_2]SO_4$[22] and $[La_2O_2]CrO_4$ shows that the mean R−O (R = S, Cr) distances in $[La_2O_2]RO_4$ and K_2RO_4 almost equal each other.[37,38] The mean Se−O distance in K_2SeO_4 (1.63 Å[39]) is smaller compared to Cr−O of 1.65 Å in K_2CrO_4, and the geometrical criterion for the suggested $La_2O_2SeO_4$ is satisfied. However, SeO_4^{2-} has its own redox way to relieve the compressive strain by detaching one oxygen with formation of La_2SeO_5 (probably $[La_2O_2]SeO_3$) which is a very stable compound.[40] Reaction of BiOCl and K_2SeO_4 at 450 °C also leads to impure Bi_2SeO_5, not Bi_2SeO_6, the impurities probably arising from secondary reactions of Bi_2SeO_5, BiOCl, and KCl.

The secondary reactions are detrimental for the exchange processes, and the precursors should be chosen so that the byproduct were inert. Our example is the Mo/W systems where rare-earth oxyhalides cannot be used as precursors due to high stability of $Ln_3MO_6Cl_3$, and existence of multinary oxybromides and oxyiodides should be checked before testing LnOBr or LnOI instead of LnOBr.

It is worth noting, however, that exchange reactions can provide very efficient synthetic pathways even when the structural elements of the precursors are not retained in the product. For instance, a 1:1 reaction of LnOCl (Ln = La, Pr) and $K_2Cr_2O_7$ yields $KLn(CrO_4)_2$ within 48 h at 500−550 °C, while reference data[41] suggest a more that 1 month annealing of Ln_2O_3 and $K_2Cr_2O_7$ at 150 °C.

Are the Reactions Truly Topochemical? The least understood issue is the mechanism of the exchange reactions. Though the products in most cases contain the structural units of precursors, it is unlikely that all these reactions are topotactic. First, the H-forms of $[Ln_2O_2]CO_3$ compounds contain $[Ln_2O_2]$ layers with a *trigonal* network of OLn_4 tetrahedra while in the structure of the $[Ln_2O_2]Cl_2$ precursors, the network is *tetragonal*. Both networks have nothing common in their topology, and rearrangement of Ln−O bonds is necessary. Second, the reaction of isostructural PbFCl and BaFCl involves amorphous intermediates. Third, reaction of $[Bi_2O_2]Cl_2$ and $Na_2[Ln_2Ti_2O_8]$ results in the $[Bi_{2-x}Ln_xO_2][Ln_{2-x}Bi_xTi_2O_8]$[10] though a “pure” exchange mechanism provides no chance for *intra*layer cation exchange ($Bi^{3+} \leftrightarrow Ln^{3+}$). It is most likely that only low-temperature reactions are truly topotactic, e.g., $CuCl_2 + K[Ca_2Nb_3O_{10}] \rightarrow KCl + CuCl[Ca_2Nb_3O_{10}]$.[11] In the meantime, in successful cases, the structure of the products retains the geometry of the precursors *as if* the reaction mechanism were topotactic.

In conclusion, exchange reactions have been shown to lead to several new metastable compounds and sufficiently simplify synthesis conditions for some known ones. Though the reaction mechanism is yet not established, new complex metastable compounds can be obtained from appropriately chosen precursors. Successful results have been observed if geometrical parameters of the assembling layers were close, if the byproduct were inert and no melt was formed, and if no redox reactions were involved.

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Supporting Information Available: X-ray crystallographic file in CIF format for the structure determination of La_2CrO_6 and Rietveld plot for Nd_2CrO_6 (raw X-ray data). This material is available free of charge via the Internet at http://pubs.acs.org.

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