

A Convenient Route for the Synthesis of Complex Metal Oxides Employing Solid-Solution Precursors

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Synthesis of complex metal oxides by the thermal decomposition of solid-solution precursors (formed by isomorphous compounds of component metals) has been investigated since the method enables mixing of cations on an atomic scale and drastically reduces diffusion distances to a few angstroms. Several interesting oxides such as $\text{Ca}_2\text{FeO}_{3.5}$, CaCo_2O_4 , $\text{Ca}_2\text{Co}_2\text{O}_5$, and $\text{Ca}_2\text{FeCoO}_5$ have been prepared by this technique starting from carbonate solid solutions of the type $\text{Ca}_{1-x}\text{Fe}_x\text{CO}_3$, $\text{Ca}_{1-x}\text{Co}_x\text{CO}_3$, and $\text{Ca}_{1-x-y}\text{M}_x\text{M}'_y\text{CO}_3$ ($\text{M}, \text{M}' = \text{Mn}, \text{Fe}, \text{Co}$). The method has been extended to oxalate solid-solution precursors, and the possibility of making use of other kinds of precursor solid solutions is indicated.

Introduction

Complex metal oxides are traditionally prepared by the ceramic method, which involves reacting oxides, carbonates, or other compounds of the component metals with repeated grinding and heating. These reactions are generally slow because of the large diffusion distances ($\sim 100\,000$ Å) and do not always yield single-phase products of the required stoichiometry. In order to decrease the diffusion distance in the ceramic method, starting materials of small particle size prepared by coprecipitation or freeze-drying have been employed, but even then the distances remain around 500 Å. Among the alternative strategies that one can employ to synthesize complex metal oxides, the solid-solution-precursor method¹ holds much promise. This method not only allows mixing of the different metal species on an atomic scale but also reduces the diffusion distance to ~ 10 Å, immaterial of the particle size. In the case of oxides containing more than one metal, the method also enables a good control over the relative proportions of the cations.

We considered it most valuable to explore the use of the solid-solution-precursor method for the synthesis of complex metal oxides, in some detail. For this purpose, we have made use of the fact that MnCO_3 , FeCO_3 , CoCO_3 , and NiCO_3 all possess the calcite structure of CaCO_3 . We have been able to synthesize several oxides containing calcium and one or more of these transition-metal ions starting from the carbonate solid solutions. We have specifically concentrated on the complex oxides containing calcium, iron, and cobalt, the calcium-manganese system having been examined earlier by Longo and Horowitz¹. As part of the study, we have characterized the carbonate precursors as well as some of the interesting metal oxides obtained by the thermal decomposition of the precursors. Since oxalates of Mg, Mn, Fe, Co, Ni, and Zn are isomorphous, we have prepared precursor-solid-solution oxalates for the first time. These solid solutions were then decomposed to obtain oxide spinels. The present study clearly illustrates the versatility of the solid-solution-precursor method for preparing complex metal oxides and suggests the need for further studies to fully exploit the method.

Experimental Section

We first tried to prepare the carbonate solid solutions $\text{Ca}_{1-x}\text{Fe}_x\text{CO}_3$ according to the method of Longo and Horowitz¹ by adding an aqueous solution of calcium and iron(II) nitrates, taken in the appropriate molar ratio, to a large excess of ~ 2 M ammonium carbonate in an atmosphere of CO_2 . We could obtain single-phase solid solution only when the composition was around $x = 0.33$. For higher values of x , quantitative precipitation of iron did not occur.

We therefore had to modify the procedure to obtain carbonate solid-solution precursors not only of the calcium-iron system but also

Table I. Crystallographic Data for Calcite-Type Carbonate Solid-Solution Precursors

no.	compn	a_R , Å	α , deg	V , Å ³
1	$\text{Ca}_2\text{Fe}(\text{CO}_3)_3$	6.161	46.4	510
2	$\text{Ca}_3\text{Fe}_2(\text{CO}_3)_5$	6.152	46.6	502
3	$\text{CaFe}(\text{CO}_3)_2$	6.065	46.5	496
4	$\text{CaFe}_2(\text{CO}_3)_3$	5.998	46.9	474
5	$\text{CaFe}_4(\text{CO}_3)_5$	5.898	47.5	459
6	$\text{CaFe}_{12}(\text{CO}_3)_{13}$	5.857	47.7	452
7	FeCO_3	5.801	47.7	440
8	$\text{CaCo}(\text{CO}_3)_2^a$	5.753	48.1	435
9	$\text{CaCo}_2(\text{CO}_3)_3^a$	5.815	47.7	443
10	$\text{Ca}_2\text{FeCo}(\text{CO}_3)_4$	6.031	47.3	493
11	$\text{Ca}_2\text{MnFe}(\text{CO}_3)_4$	6.158	46.6	507
12	$\text{Ca}_2\text{MnCo}(\text{CO}_3)_4$	6.071	47.1	494

^a There are additional lines in the X-ray diffraction pattern that are probably due to ordering of calcium and cobalt in the calcite structure.

of other systems such as $\text{Ca}_{1-x}\text{Co}_x\text{CO}_3$, $\text{Ca}_{1-x-y}\text{Co}_x\text{Fe}_y\text{CO}_3$, $\text{Ca}_{1-x-y}\text{Mn}_x\text{Co}_y\text{CO}_3$, and $\text{Ca}_{1-x-y}\text{Mn}_x\text{Fe}_y\text{CO}_3$. In the modified procedure an aqueous solution of the metal nitrates (0.5 M) containing appropriate molar amounts of the metal ions was added dropwise to a hot (~ 80 °C) solution of 1 M sodium bicarbonate with constant stirring, passing CO_2 through the solution continuously. The pH of the solution was around 8.5 when precipitation occurred. The precipitated carbonate was washed with distilled water and dried under vacuum. The colorless filtrate was tested for residual metal ions to determine whether precipitation was complete.

Oxalate solid-solution precursors containing two or more of the divalent metal ions Mn, Co, Ni, or Zn were prepared by adding ~ 0.5 M aqueous solutions of divalent metal acetates to a hot solution of 1 M oxalic acid under stirring. Precipitation was nearly quantitative in all the cases studied.

The precursors were characterized by X-ray powder diffraction, differential thermal analysis, and infrared spectroscopy. X-ray powder diffraction patterns were recorded with a Philips powder diffractometer (PW 1050/70) employing iron-filtered $\text{Co K}\alpha$ radiation. Infrared spectra were recorded in KBr pellets on a Perkin-Elmer 580 infrared spectrometer.

For the preparation of complex metal oxides, the precursors were heated above their decomposition temperatures (≥ 400 °C) in an atmosphere of air or flowing oxygen. Reaction times varied between 1 and 48 h. Products were examined by X-ray powder diffraction. Oxidation states of reducible cations, where essential, were determined by the oxalate method or iodometric method. In the calcium-cobalt system, compositions of the oxides were checked by quantitative analyses of calcium and cobalt by standard analytical methods.

Results and Discussion

Carbonate Solid-Solution Precursors. Several carbonate solid-solution precursors containing calcium and one or more of the divalent transition-metal ions Mn, Fe, or Co were characterized by X-ray powder diffraction, infrared spectroscopy, and differential thermal analysis. Compositions of the precursors together with their unit cell dimensions are listed in Table I. The precursors investigated by us in the $\text{Ca}_{1-x}\text{Fe}_x\text{CO}_3$ system were those with $x = 1/3, 2/5, 1/2, 2/3, 4/5$,

(1) (a) H. S. Horowitz and J. M. Longo, *Mater. Res. Bull.*, **13**, 1359 (1978); (b) J. M. Longo and H. S. Horowitz in "Preparation and Characterization of Materials", J. M. Honig and C. N. R. Rao, Eds., Academic Press, New York, 1981, p 29.

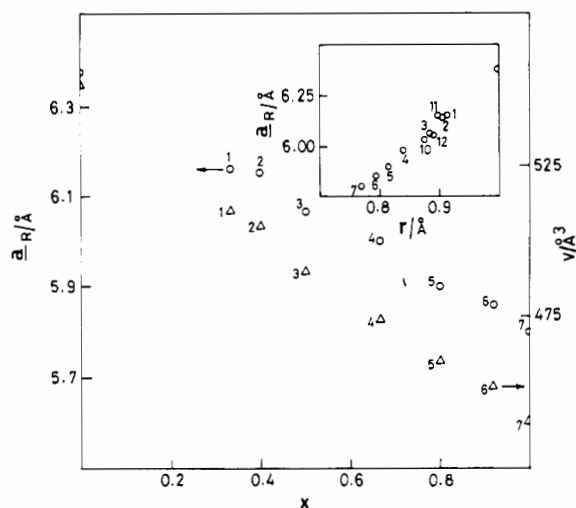


Figure 1. Plots of the rhombohedral parameter, a_R (circles), and the unit cell volume, V (triangles), of the calcite-type carbonate solid solutions, $\text{Ca}_{1-x}\text{Fe}_x\text{CO}_3$, against x . A plot of a_R vs. weighted mean cation radius, r , for the various calcite-type carbonate solid solutions listed in Table I is shown in the insert. The numbers refer to the compositions given in Table I.

and $^{12}/_{13}$ corresponding to the formulas $\text{Ca}_2\text{Fe}(\text{CO}_3)_3$, $\text{Ca}_3\text{Fe}_2(\text{CO}_3)_5$, $\text{CaFe}(\text{CO}_3)_2$, $\text{CaFe}_2(\text{CO}_3)_3$, $\text{CaFe}_4(\text{CO}_3)_5$, and $\text{CaFe}_{12}(\text{CO}_3)_{13}$, respectively. All of them are single-phase compounds crystallizing in the rhombohedral calcite structure. The rhombohedral parameter, a_R , as well as the unit cell volume, V , of these phases varies smoothly with x as shown in Figure 1. Infrared absorption spectra of these carbonates are typical of the calcite structure,² showing absorption bands around 1450, 1080, 870, and 720 cm^{-1} due to the ν_3 , ν_1 , ν_2 , and ν_4 modes, respectively, of the carbonate ion. Decomposition temperatures of the precursors were considerably lower than that of CaCO_3 (900 °C); thus, the decomposition temperatures of the $x = 1/3$ and $1/2$ samples were 690 and 620 °C, respectively.

In the $\text{Ca}_{1-x}\text{Co}_x\text{CO}_3$ system, we have prepared two single-phase precursors with $x = 1/2$ and $1/3$, both possessing calcite-related structures and exhibiting lower decomposition temperatures than CaCO_3 . More interestingly, we have been able to synthesize ternary carbonate solid solutions of the formulas $\text{Ca}_2\text{FeCo}(\text{CO}_3)_4$, $\text{Ca}_2\text{MnFe}(\text{CO}_3)_4$, and $\text{Ca}_2\text{MnCo}(\text{CO}_3)_4$, all of which crystallize in the calcite structure. The rhombohedral a_R of all the solid-solution precursors increases systematically with the weighted mean cation radius³ as shown in the insert of Figure 1.

Formation of complex metal oxides from the precursors was investigated by heating them in air or in oxygen above their decomposition temperatures for varying durations and examining the products by X-ray diffraction. As the cations are mixed in an atomic scale in these precursors, almost instantaneous reaction occurs after decomposition to give the product oxides. For examples, the two well-known oxides^{4,5} $\text{Ca}_2\text{Fe}_2\text{O}_5$ and CaFe_2O_4 in the Ca-Fe-O system could be obtained by heating the corresponding precursor solid solutions in air at 800 and 1000 °C, respectively, for about 1 h. The unit cell parameters $a = 5.425$, $b = 14.768$, and $c = 5.598$ Å for

Table II. X-ray Powder Diffraction Data for $\text{Ca}_2\text{FeO}_{3.5}$

hkl	$d_{\text{obsd.}} \text{ \AA}$	I/I_0	$d_{\text{calcd.}}^a \text{ \AA}$
020	6.86	58	6.86
400	3.693	14	3.698
004	3.058	11	3.048
142	2.931	14	2.929
114			2.917
204	2.797	17	2.818
340			2.815
431			2.798
520	2.714	78	2.716
413	2.675	22	2.682
051			2.676
342	2.557	100	2.556
060	2.281	11	2.286
602			2.286
700	2.127	19	2.113
540	2.227	31	2.240
352			2.231
006	2.032	10	2.032
070	1.957	25	1.959
171	1.918	32	1.918
730			1.918
462	1.848	11	1.852
800			1.849
670	1.535	28	1.534
931			1.534
0,10,0	1.372	14	1.371

^a $a = 14.79$ (2) Å, $b = 13.71$ (2) Å, $c = 12.19$ (1) Å.

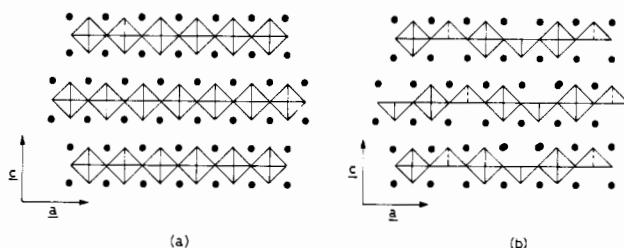


Figure 2. Possible ordering of anion vacancies in $\text{Ca}_2\text{FeO}_{3.5}$: (a) K_2NiF_4 structure; (b) $\text{Ca}_2\text{FeO}_{3.5}$ structure.

$\text{Ca}_2\text{Fe}_2\text{O}_5$ and $a = 3.024$, $b = 10.705$, and $c = 9.230$ Å for CaFe_2O_4 , obtained by X-ray powder patterns agree with the values reported in the literature.^{5,6} There were no additional lines in the X-ray diffraction patterns due to either Fe_2O_3 or CaO , indicating the single-phase nature of the complex oxides formed. We decomposed $\text{CaFe}(\text{CO}_3)_2$ at the lowest possible temperature (650 °C) in flowing oxygen in order to determine whether any CaFeO_{3-x} with $x < 0.5$ is formed. The X-ray diffraction pattern of the product obtained after heating for 1 h showed characteristic lines due to brownmillerite $\text{Ca}_2\text{Fe}_2\text{O}_5$ and the undecomposed calcite-type precursor. Decomposition of $\text{Ca}_2\text{Fe}(\text{CO}_3)_3$ at 750 °C for ~6 h yielded a new phase that contained iron in the 3+ state. The product, identified as $\text{Ca}_2\text{FeO}_{3.5}$, showed an X-ray diffraction pattern (Table II) different from that of either $\text{Ca}_2\text{Fe}_2\text{O}_5$ or CaFe_2O_4 . The pattern could be indexed on the basis of an orthorhombic cell with $a = 14.79$ (2), $b = 13.71$ (2), and $c = 12.19$ (1) Å. $\text{Ca}_2\text{FeO}_{3.5}$ may be regarded as an anion-deficient variant of Ca_2FeO_4 that is likely to possess a K_2NiF_4 -type structure similar to Ca_2MnO_4 . $\text{Ca}_2\text{MnO}_{3.5}$, which is also an anion-deficient oxide of the K_2NiF_4 family, has been recently reported by Poeppelmeier et al.⁷ The X-ray diffraction pattern and unit cell parameters of $\text{Ca}_2\text{FeO}_{3.5}$ are quite different from those of $\text{Ca}_2\text{MnO}_{3.5}$. We suggest that the ordering of anion

(2) S. D. Ross, "Inorganic Infrared and Raman Spectra", McGraw-Hill, London, 1972, p 144.

(3) The weighted mean cation radius, r , of a precursor $\text{A}_n\text{B}_m(\text{CO}_3)_p$ has been calculated as $(nr_A + mr_B)/(n + m)$ where r_A and r_B represent effective ionic radii of A and B, respectively, in six-coordination. Ionic radii were taken from R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B*, **B25**, 925 (1969).

(4) A. D. Wadsley in "Nonstoichiometric Compounds", L. Mandelcorn, Ed., Academic Press, New York, 1964, p 134.

(5) A. F. Reid, *Inorg. Chem.*, **6**, 631 (1967).

(6) (a) E. F. Bertaut, P. Blum, and A. Sagnieres, *Acta Crystallogr.*, **12**, 149 (1959); (b) J. Berggren, *Acta Chem. Scand.*, **25**, 3616 (1971).

(7) (a) K. R. Poeppelmeier, M. E. Leonowicz, and J. M. Longo, *J. Solid State Chem.*, **44**, 89 (1982); (b) K. R. Poeppelmeier, M. E. Leonowicz, J. C. Scanlon, J. M. Longo, and W. B. Yelon, *Ibid.*, **45**, 71 (1982).

Table III. X-ray Powder Diffraction Data for $\text{Ca}_2\text{Co}_2\text{O}_5$

<i>hkl</i>	$d_{\text{obsd.}}^a, \text{\AA}$	I/I_0	$d_{\text{calcd.}}^a, \text{\AA}$
020	5.367	100	5.371
030	3.575	43	3.581
022	3.070	26	3.069
122	2.952	37	2.958
410	2.693	43	2.693
222	2.688	80	{2.687
040			{2.686
330	2.556	14	2.576
240	2.410	94	2.418
203	2.277	57	2.275
402	2.227	17	2.232
050	2.146	14	2.148
303	2.079	47	{2.069
422			{2.061
441	1.870	33	{1.871
004			{1.870
043	1.823	3	1.827
060	1.790	9	1.790
061	1.740	9	1.741
442	1.723	17	1.717
630	1.652	13	1.647
253	1.560	9	{1.562
262			{1.551
005	1.496	6	{1.496
424			{1.491
642	1.413	6	1.413
650	1.398	11	{1.404
462			{1.397
800	1.390	11	1.391

$a = 11.12 (1) \text{\AA}$, $b = 10.74 (1) \text{\AA}$, $c = 7.48 (1) \text{\AA}$.

vacancies in the iron compound is different from that in the manganese compound just as the ordering in $\text{CaFeO}_{2.5}$ and $\text{CaMnO}_{2.5}$ is different⁷. It is likely that the ordering of anion vacancies in $\text{Ca}_2\text{FeO}_{3.5}$ is similar to that in the brownmillerite structure consisting of alternating rows of octahedra and tetrahedra in the perovskite-like layers of K_2NiF_4 structure. We have illustrated the proposed vacancy ordering scheme in Figure 2.

In the Ca-Co-O system we have synthesized two new oxides, $\text{Ca}_2\text{Co}_2\text{O}_5$ and CaCo_2O_4 , by decomposing the appropriate precursors in an oxygen atmosphere at 650 and 700 °C, respectively, for 6 h. Chemical analyses showed that cobalt was in the 3+ state in both phases and that calcium and cobalt were in the required ratios. The X-ray diffraction pattern of $\text{Ca}_2\text{Co}_2\text{O}_5$ (Table III) bears some resemblance to that of $\text{Ca}_2\text{Mn}_2\text{O}_5$ and could be indexed on the basis of an orthorhombic unit cell with $a = 11.12 (1)$, $b = 10.74 (1)$, and $c = 7.48 (1) \text{\AA}$. Comparison of these parameters with those of $\text{Ca}_2\text{Mn}_2\text{O}_5$ reveals doubling of the a and c parameters in the cobalt compound. Poepelmeier et al.⁷ have shown that anion vacancies in $\text{Ca}_2\text{Mn}_2\text{O}_5$ order in alternate (110) planes of the cubic perovskite structure, resulting in a square-pyramidal coordination around manganese. In $\text{Ca}_2\text{Co}_2\text{O}_5$, a similar vacancy ordering may be present, but the doubling of the c parameter would indicate that the (110) rows of anions and anion vacancies alternate along the c direction as shown in Figure 3.

The X-ray diffraction pattern of CaCo_2O_4 (Table IV) is unique in the sense that it does not match with the structures of any of the known AB_2O_4 oxides⁸. An earlier report⁹ that CaCo_2O_4 crystallizes in the spinel structure therefore seems to be in error. On the other hand, the X-ray pattern is somewhat similar to that of the P2- and P3-type Na_xCoO_2

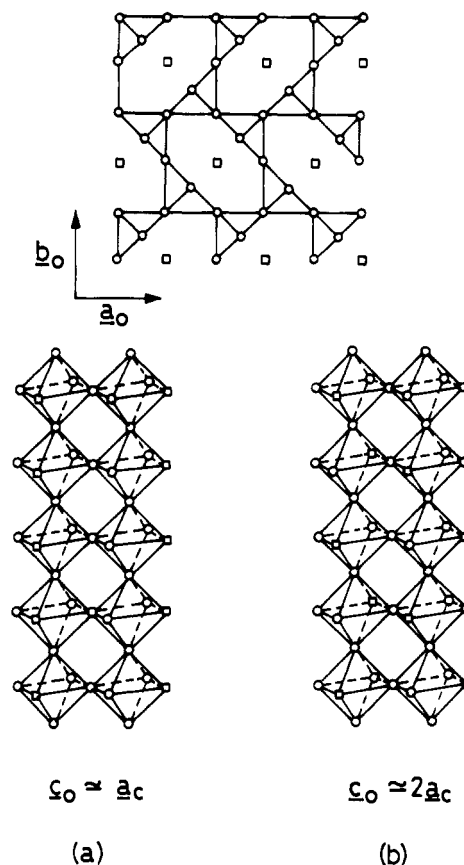


Figure 3. Comparison of ordering of anion vacancies: (a) $\text{Ca}_2\text{Mn}_2\text{O}_5$ structure; (b) $\text{Ca}_2\text{Co}_2\text{O}_5$ structure (partially adopted from ref 7). The ab plane of both oxides is shown at the top. Vacancies are indicated by squares.

Table IV. X-ray Powder Diffraction Data for CaCo_2O_4

<i>hkl</i>	$d_{\text{obsd.}}^a, \text{\AA}$	I/I_0	$d_{\text{calcd.}}^a, \text{\AA}$
200	5.432	100	5.430
101	3.713	14	3.728
30 $\bar{1}$	3.458	6	3.417
40 $\bar{1}$	2.742	13	2.758
400	2.715	33	2.715
021	2.416	32	2.413
22 $\bar{1}$	2.359	22	2.366
102	2.343	42	2.350
002	2.233	9	2.238
31 $\bar{2}$	2.106	5	{2.107
402			{2.098
221	2.079	4	2.073
420	1.972	39	{1.971
41 $\bar{2}$			{1.970
112	1.952	54	1.940
131	1.692	14	1.700
122	1.675	10	{1.674
302			{1.673
203	1.574	5	1.577
430	1.559	10	{1.562
700			{1.551
432	1.415	27	1.413
800	1.358	9	1.358

$a = 11.50 (2) \text{\AA}$, $b = 5.73 (1) \text{\AA}$, $c = 4.74 (1) \text{\AA}$, $\beta = 109.2 (2)^\circ$.

phase¹⁰. We could index the pattern satisfactorily on the basis of a monoclinic unit cell with $a = 11.50 (2) \text{\AA}$, $b = 5.73 (1) \text{\AA}$, $c = 4.74 (1) \text{\AA}$, and $\beta = 109.2 (2)^\circ$. These cell parameters bear a close resemblance to those of $\text{Ca}_2\text{Mn}_3\text{O}_8$ reported by

(8) O. Muller and R. Roy, "The Major Ternary Structural Families", Springer-Verlag, Berlin, 1974, pp 15-82.

(9) T. V. Andrushkevich, L. M. Plyasova, A. Ostankovich, G. K. Borekoo, L. M. Kefeli, V. V. Popovskii, and E. D. Grazhdannikov, *Izv. Akad. Nauk SSSR, Sib. Ord., Inst., Katal.*, **3**, 333 (1965); *Chem. Abstr.*, **68**, 26382e (1968).

(10) (a) C. Fouassier, G. Matejka, J. M. Reau, and P. Hagenmuller, *J. Solid State Chem.*, **6**, 532 (1973); (b) C. Delmas, C. Fouassier, and P. Hagenmuller, *Physica B+C (Amsterdam)*, **99B+C**, 81 (1980).

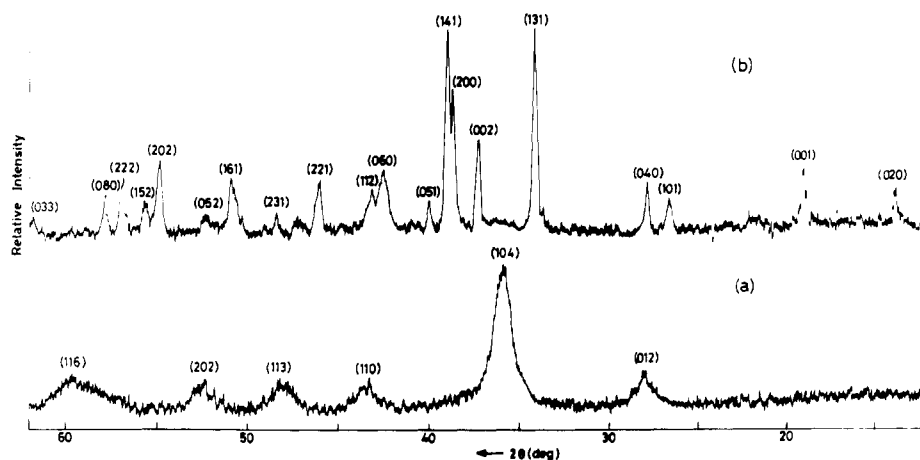


Figure 4. X-ray powder diffraction patterns: (a) $\text{Ca}_2\text{FeCo}(\text{CO}_3)_4$; (b) $\text{Ca}_2\text{FeCoO}_5$. In (a), the lines are broad probably due to small crystallite size.

Ansell et al.¹¹ The latter crystallizes in a layer structure consisting of Mn_3O_8 layers formed by close packing of the oxygen atoms in the sequence ABCCA...; between the alternate oxygen planes, three-fourths of the possible octahedral sites are occupied by manganese, the calcium atoms being present in the trigonal-prismatic sites between the Mn_3O_8 layers. The structure of CaCo_2O_4 may be derived from the $\text{Ca}_2\text{Mn}_3\text{O}_8$ structure by filling with cobalt *all* the octahedral sites between alternate oxygen planes in the ABCC sequence.

We have obtained three new oxides possessing perovskite-related structures by the thermal decomposition of the ternary precursor carbonates $\text{Ca}_2\text{FeCo}(\text{CO}_3)_4$, $\text{Ca}_2\text{MnFe}(\text{CO}_3)_4$, and $\text{Ca}_2\text{MnCo}(\text{CO}_3)_4$. Decomposition of $\text{Ca}_2\text{FeCo}(\text{CO}_3)_4$ in oxygen at 650 °C for 6 h yielded $\text{Ca}_2\text{FeCoO}_5$. The X-ray diffraction pattern shown in Figure 4 could be indexed on the basis of the brownmillerite structure with $a = 5.403$ (9), $b = 14.79$ (2), and $c = 5.59$ (1) Å. In this oxide, it is quite likely that the Fe^{3+} and Co^{3+} ions occupy the tetrahedral and the octahedral sites, respectively, of the brownmillerite structure⁶. It is significant that substitution of iron in $\text{Ca}_2\text{Fe}_2\text{O}_5$ by cobalt could not be achieved beyond 25 mol % by direct solid-state reaction¹².

Heating the precursor $\text{Ca}_2\text{MnFe}(\text{CO}_3)_4$ at 900 °C for 20 h in oxygen yielded a cubic perovskite-type phase. When the sample was heated at 1200 °C for 24 h, there was no change in the X-ray diffraction pattern excepting that the lines became sharper. Chemical analysis of the oxidation state of the transition metals revealed the composition to be $\text{Ca}_2\text{MnFeO}_{5.64 \pm 0.03}$, brownmillerite that about 5% of the anion sites are vacant. On the basis of X-ray diffraction, we were not able to detect any ordering of vacancies in this phase and the pattern could be indexed on a cubic perovskite cell with $a = 3.773$ (1) Å. ABO_{3-x} phases are known to crystallize in the cubic perovskite structure¹³ when $x \leq 0.25$ probably because the vacancies are not ordered in the long range; thus, $\text{Ca}_2\text{FeTiO}_{5.5}$ and $\text{Ca}_2\text{Fe}_{0.8}\text{Mn}_{1.2}\text{O}_{6-y}$ are known to be cubic perovskites.^{13,14}

Reaction of the precursor $\text{Ca}_2\text{MnCo}(\text{CO}_3)_4$ at 950 °C in an oxygen atmosphere for 10 h yielded a new phase. X-ray diffraction pattern of this phase (Table V) showed some sim-

Table V. X-ray Powder Diffraction Data for $\text{Ca}_3\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_{8-y}$

<i>hkl</i>	d_{obsd} , Å	I/I_0	d_{calcd} , ^a Å
004	5.60	11	5.62
110	4.76	11	4.73
111	4.60	72	4.63
130	2.900	16	2.901
131	2.880	25	2.877
126	2.646	100	2.637
043	2.475	37	2.454
206	2.167	16	2.166
046	2.134	6	2.135
129	2.053	9	2.072
146	1.958	29	1.981
054	1.940	29	1.949
1,1,12	1.733	5	1.741
1,2,12	1.677	12	1.672
1,3,12	1.578	11	1.573
2,0,12	1.530	12	1.530
166	1.490	15	1.507
260	1.451	9	1.451
400	1.325	11	1.328

^a $a = 5.310$ (8) Å, $b = 10.39$ (1) Å, $c = 22.47$ (3) Å.

ilarity to $\text{Ca}_2\text{LaFe}_3\text{O}_8$ ¹⁵ and could be satisfactorily indexed on a perovskite-related cell with $a = 5.310$ (8), $b = 10.39$ (1), and $c = 22.47$ (3) Å. The relationship between the orthorhombic cell of this phase and the cubic perovskite subcell could be $a_0 \approx (2^{1/2})a_c$, $b_0 \approx 2(2^{1/2})a_c$, and $c_0 = 6a_c$. Such a supercell may be taken to indicate an ordering of anion vacancies similar to that in $\text{Ca}_2\text{LaFe}_3\text{O}_8$ where two-thirds of iron atoms are in octahedral (O) sites and one-third in tetrahedral (T) sites,¹⁵ the sequence of polyhedra along the c axis being OOTOOT... Chemical analysis of the oxidation state of transition metals in the new phase showed the composition to be $\text{Ca}_2\text{MnCoO}_{5.16 \pm 0.02}$. This composition is close to $\text{A}_2\text{M}_2\text{O}_{5.20}$, which would correspond to the $n = 2.5$ phase in the $\text{A}_n\text{B}_n\text{O}_{3n-1}$ series; an example is provided by $\text{Ca}_5\text{Fe}_4\text{TiO}_{13}$ reported by Grenier et al.¹⁶ We must point out however that it is rather difficult to arrive at the cation distribution in $\text{Ca}_2\text{MnCoO}_{5.16 \pm 0.02}$ based on the present studies.

Oxalate Solid-Solution Precursors. Unlike in the case of carbonates, no oxalate solid-solution precursor has been reported in the literature. We have prepared a few oxalate solid solutions containing two or more of the divalent metal ions

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Table VI. Crystallographic Data for Oxalate Precursors and Their Product Spinel-Type Oxides

compn	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	β , deg	complex oxide	<i>a</i> , Å
ZnCo ₂ (C ₂ O ₄) ₃ ·6H ₂ O	9.826	5.428	9.841	105.7	ZnCo ₂ O ₄	8.109
NiCo ₂ (C ₂ O ₄) ₃ ·6H ₂ O	9.809	5.408	9.830	105.8	NiCo ₂ O ₄	8.130
ZnNiCo(C ₂ O ₄) ₃ ·6H ₂ O	9.821	5.403	9.871	106.0	ZnNiCoO ₄	8.172
ZnNiMn(C ₂ O ₄) ₃ ·6H ₂ O	9.805	5.465	9.900	105.6	ZnNiMnO ₄	8.318

Mn, Co, Ni, and Zn. Compositions and unit cell parameters of these are listed in Table VI. All of them are isostructural, possessing the humboldtine¹⁷ structure of FeC₂O₄·2H₂O. The oxalate solid solutions decompose at considerably lower temperatures (below 400 °C) than the carbonates. This low temperature of decomposition has enabled us to obtain stoichiometric oxides as single-phase materials. The various spinel-type oxides obtained by decomposition of the oxalate precursors in oxygen atmosphere are given in Table VI. Of the four spinel oxides prepared by us, ZnCoNiO₄ is a new compound reported for the first time. Such an oxide containing cobalt and nickel in the 3+ oxidation state cannot be prepared by the ceramic method.

Concluding Remarks

The present study clearly establishes that the solid-solution-precursor method provides a convenient route for the synthesis of complex metal oxides. The method not only yields single-phase materials of known phases at relatively low temperatures but also enables the preparation of new oxides. Although we have prepared only a few ternary oxides in the Ca-Fe-O system, it should be possible to prepare many other novel oxides such as CaFe₂O₄(FeO)_{*n*}¹⁸ or CaFe₄O₇ by employing controlled conditions. Similarly, in the quaternary Ca-M-M'-O systems (M ≠ M' = Mn, Fe, Co), synthesis of several interesting oxides is clearly possible. Carbonate solid-solution precursors containing Mg, Sr, Zn, or Cd along with divalent transition-metal ions may provide routes to prepare several oxides, but not all the combinations of these metal ions may readily form insoluble carbonates.

Other types of solid-solution precursors are also worth exploring, the most obvious ones being those involving nitrates and hydroxides. The nitrate solid-solution precursors are particularly important since they would decompose at low temperatures, yielding active oxides. Structural considerations

indicate that it should be possible to prepare such nitrate solid solutions incorporating many of the transition-metal ions. Thus, decomposition of solid solutions of cobalt and nickel nitrates would give rise to oxides of the general formula Co_{3-x}Ni_xO₄, which cannot be prepared by the ceramic method. NiCo₂O₄ has indeed been reported¹⁹ to be formed by the decomposition of nitrate mixtures, but without realizing that a solid solution had been formed during the preparation.

It is noteworthy that nitrates of Ca, Sr, Ba, and Pb are isostructural, and it should be possible to prepare compounds such as BaPbO₃ and Sr₂PbO₄ by the decomposition of the corresponding nitrate solid solutions. It is not essential for the two component salts to be isomorphous in order to be able to prepare precursor solid solutions; it should be possible in many instances to obtain single-phase precursor solid solutions by employing appropriate conditions. For example, studies in this laboratory indicate that it is possible to prepare hydroxide solid-solution precursors of La, Al, Co, Ni, and so on. The solid solution La_{0.5}M_{0.5}(OH)₃ (M = Co, Ni) possessing the La(OH)₃ structure can be precipitated by employing alkaline hypochlorite while Ln_{0.5}Al_{0.5}(OH)₃ (Ln = rare earth) can be obtained by simple alkaline hydrolysis of a solution containing an appropriate mixture of the component salts. By suitable combinations of metal ions, one can readily prepare complex quaternary oxides possessing interesting electronic and magnetic properties by the hydroxide solid-solution-precursor route. We are continuing to investigate several other precursor solid solutions including nitrates, hydroxides, and cyanides.

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Registry No. Ca₂FeO_{3.5}, 12049-92-2; Ca₂Co₂O₅, 51373-88-7; CaCo₂O₄, 12323-37-4; ZnCo₂O₄, 12187-36-9; NiCo₂O₄, 12017-35-5; ZnNiCoO₄, 53682-27-2; ZnNiMnO₄, 12214-35-6; Ca₂Fe₂O₅, 12013-62-6; CaFe₂O₄, 12013-33-1.

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