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Synthesis of Complex Metal Oxides Using Hydroxide, Cyanide, and Nitrate Solid Solution Precursors*

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Precursor solid solutions provide convenient routes for preparing complex metal oxides. Hydroxide solid solutions of the general formula $Ln_{1-x}M_x(OH)_3$ (where Ln = La or Nd and M = Al, Cr, Fe, Co, or Ni) and $La_{1-x-y}M'_xM''_y(OH)_3$ (where M' = Ni and M'' = Co or Cu) crystallize in the rare earth trihydroxide structure and can be decomposed at relatively low temperatures to yield complex metal oxides. Several oxides of the type $LaNiO_3$, $NdNiO_3$, $LaNi_{1-x}Co_xO_3$, and $LaNi_{1-x}Cu_xO_3$ have been prepared by the hydroxide precursor route. Thermal decomposition of cyanide precursors of the type $Ln[M_{1-x}M'_x(CN)_6] \cdot 5H_2O$ and $Ln_{1-x}Ln'_x[M(CN)_6] \cdot 5H_2O$ yields the quaternary oxides which are not readily made by ceramic methods. Nitrate solid solution precursors of the type $Ba_{1-x}Pb_x(NO_3)_2$, $Sr_{1-x}Pb_x(NO_3)_2$, and $BaSrPb(NO_3)_6$ have been used for preparing several interesting oxides such as $BaPbO_3$, Ba_2PbO_4, and $BaSrPbO_4$.

Introduction

It has been shown recently that carbonate solid solution precursors provide a convenient route for the preparation of novel metal oxides (*1*, *2*). Accordingly, starting with $Ca_{1-x}M_xCO_3$ (M = Mn, Fe, Co) solid solutions of calcite structure, a number of ternary and quaternary oxides have been synthesized. The solid solution precursor method reduces diffusion distances to a few angstroms compared to 100,000 Å in the ceramic method and ensures better homogeneity of the oxides obtained by decomposition of the precursors. We considered it most worthwhile to systematically examine whether the solid solution precursor method can be extended to other systems, besides carbonates and oxalates (*2*). Isostructural series of inorganic solids such as the cyanides, hydroxides and nitrates could indeed be potentially useful as precursors in solid-state synthesis. For example, barium titanium citrate is pyrolyzed to prepare stoichiometric and homogeneous $BaTiO_3$.

We have explored the possibility of using complex metal hydroxides and cyanides consisting of rare earth and transition metal atoms for the synthesis of ternary and quaternary metal oxides. In this process, we have discovered the formation of a series of ternary and quaternary hydroxides of the formulas $Ln_{1-x}M_x(OH)_3$ [Ln = La or Nd; M = Al, Cr, Fe, Co, or Ni] and $La_{1-x-y}M'_xM''_y(OH)_3$ [M' = Ni and M'' = Co or Cu], respectively, crystallizing in the $Ln(OH)_3$ structure. We have prepared several novel

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oxides such as $NdNiO_3$ and $LaNi_{1-x}Cu_xO_3$ by the hydroxide precursor route. We have also shown that the isostructural alkaline earth metal nitrates, $Ba(NO_3)_2$ and $Sr(NO_3)_2$, together with $Pb(NO_3)_2$ form solid solutions which could be employed as precursors for the synthesis of oxides such as $BaPbO_3$, Ba_2PbO_4, and $BaSrPbO_4$. We have been able to prepare oxides of the type $Ln_{1-x}Ln'_xMO_3$ and $LnM_{1-x}M'_xO_3$ by the decomposition of solid solutions of complex cyanides; preparation of ternary oxides of the type $LnMO_3$ by the decomposition of complex cyanides of the type $Ln[M(CN)_6] \cdot xH_2O$ has indeed been known for some time (*3*).

Experimental

The hydroxide solid solutions, $Ln_{1-x}M_x(OH)_3$ [Ln = La, Nd; M = Al, Cr, Fe, Co, or Ni] were prepared as follows. When M = Cr or Fe, the solid solutions $La_{0.5}M_{0.5}(OH)_3$ were obtained by adding an aqueous nitrate solution (1 *M*) of the metal ions in the appropriate molar ratio to a NaOH (~6 *M*) solution kept under constant stirring. The precipitated hydroxide was washed alkali-free with hot water, filtered, and then dried in air at 370 K. $La_{0.5}Al_{0.5}(OH)_3$ was similarly prepared using ammonium hydroxide as the precipitating agent. This method was, however, not applicable for the preparation of $Ln_{1-x}M_x(OH)_3$ when M = Co, Ni, or Cu for which only divalent metal nitrates are available. Hydroxide solid solutions of these metals were prepared under oxidizing conditions using a hypochlorite medium. This was done by adding an aqueous solution of metal nitrates (1 *M*) to a NaOH solution (~6 *M*) saturated with chlorine. Chlorine was passed for about 30 min even after the addition of the metal nitrate solution was complete to ensure oxidation of M^{2+} to M^{3+}. The precipitated hydroxide was filtered, washed, and dried as before. By this procedure, we could prepare $Ln_{0.5}M_{0.5}(OH)_3$ solid solutions for Ln = La or Nd, and M = Co or Ni, $La_{1-x}Ni_x(OH)_3$ with x = 0.33 and 0.67 as well as quaternary hydroxides of the type $La_{0.5}M'_{0.5-x}M''_x(OH)_3$ [M' = Ni; M'' = Co or Cu] indicating that the method is indeed a general one for the preparation of $Ln_{1-x}M_x(OH)_3$ [Ln = La, Nd; M = Co, Ni, Cu].

The nitrate solid solutions, $Ba_{1-x}Pb_x(NO_3)_2$ (x = 0.33, 0.40, 0.50, 0.67), were prepared as follows. Required amounts of $Ba(NO_3)_2$ and $Pb(NO_3)_2$ were dissolved in a minimum quantity of water. The aqueous nitrate mixture was added dropwise to a constantly stirred 13 *N* nitric acid maintained in an ice bath. The nitrate solid solution, precipitated immediately, was filtered and dried in air at room temperature. Similarly $Sr_{1-x}Pb_x(NO_3)_2$ (x = 0.33 and 0.5) and $BaSrPb(NO_3)_6$ were prepared.

The cyanide solid solution, $La[Fe_{0.5}Co_{0.5}(CN)_6] \cdot 5H_2O$, was prepared by the addition of a 0.5 *M* aqueous solution of $K_3Co(CN)_6$ and $K_3Fe(CN)_6$, taken in 1 : 1 molar ratio, to a hot (340 K) solution (0.5 *M*) of lanthanum chloride kept under constant stirring. The cyanide precipitated was washed with a minimum quantity of cold water, filtered, and then air-dried. The solid solution, $La_{0.5}Nd_{0.5}[Co(CN)_6] \cdot 5H_2O$, was prepared by adding a hot (~340 K) solution (0.5 *M*) of La and Nd chloride (1 : 1 molar ratio) to a constantly stirred $K_3Co(CN)_6$ solution (0.5 *M*).

The cyanide, hydroxide, and nitrate solid solutions were characterized by X-ray powder diffraction, differential thermal analysis, and, where required, infrared spectroscopy. For preparing the metal oxides, the precursor solid solutions were heated above their decomposition temperatures either in air or in flowing oxygen. Reaction times varied between 6 and 12 hr. The metal oxides were characterized by X-ray powder diffraction and, where essential, chemical analysis, X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, and electron diffraction. X-ray photoelectron spectra (XPS) were recorded with a ESCA III Mark 2 spectrometer of VG Scientific, England (*4*). X-ray absorption spectra (XAS) were recorded with a bent-crystal X-ray spectrograph (*5*). Electron diffraction patterns were recorded with a JEOL JEM-200 CX electron microscope.

Results and Discussion

Hydroxide Solid Solution Precursors

Synthesis of several ternary oxides, some for the first time, has been achieved by the hydroxide precursor route. The hydroxide solid solutions of the general formula $La_{1-x}M_x(OH)_3$ for M = Al, Fe or Co, x = 0.5, and for M = Ni, x = 0.33, 0.50, and 0.67, crystallize in the $La(OH)_3$ structure with the space group $P6_3/m$ (6). We have shown the X-ray diffractograms of some hydroxide solid solutions and of $La(OH)_3$ in Figs. 1 and 2 to illustrate their isostructural nature. It is significant that all the phases possess nearly the same unit cell dimensions, $a \simeq 6.53$ and $c \simeq 3.84$ Å (*7*). The solid solutions $Nd_{0.5}M_{0.5}(OH)_3$ (M = Co or Ni) prepared by us were also found to crystallize in this structure with unit cell parameters comparable to those of $Nd(OH)_3$. Compositions in the chromium system, e.g., $La_{0.5}Cr_{0.5}(OH)_3$, were, however, X-ray amorphous.

The hydroxide solid solutions decompose endothermically in air at relatively low temperatures (~620 K). Unit cell dimensions, decomposition temperatures of the hydroxide precursors, along with reaction conditions, compositions, and unit cell dimensions of the product oxides obtained are listed in Table I. The formation temperature of a $LnMO_3$ phase from its hydroxide precursor seems to depend on the nature of the metal atom M. For instance, $LaNiO_3$ was obtained almost instantaneously after the decomposition of $La_{0.5}Ni_{0.5}(OH)_3$ at as low a temperature as 670 K, while the formation of $LaAlO_3$ and $LaCoO_3$ required temperatures around 1170 K. The hydroxide precursor route enables synthesis of

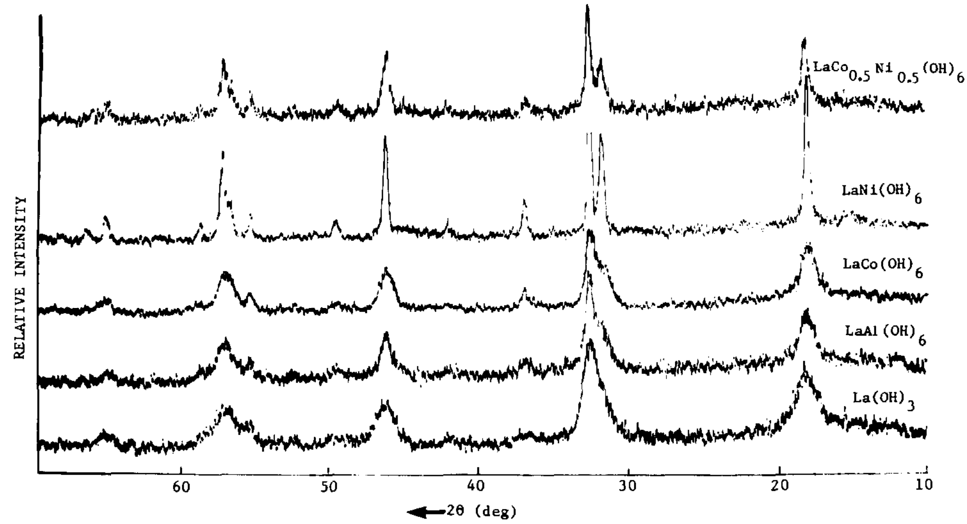

FIG. 1. X-ray powder diffraction patterns of $La(OH)_3$ and of a few precursor hydroxide solid solutions (λ = 1.7902 Å).

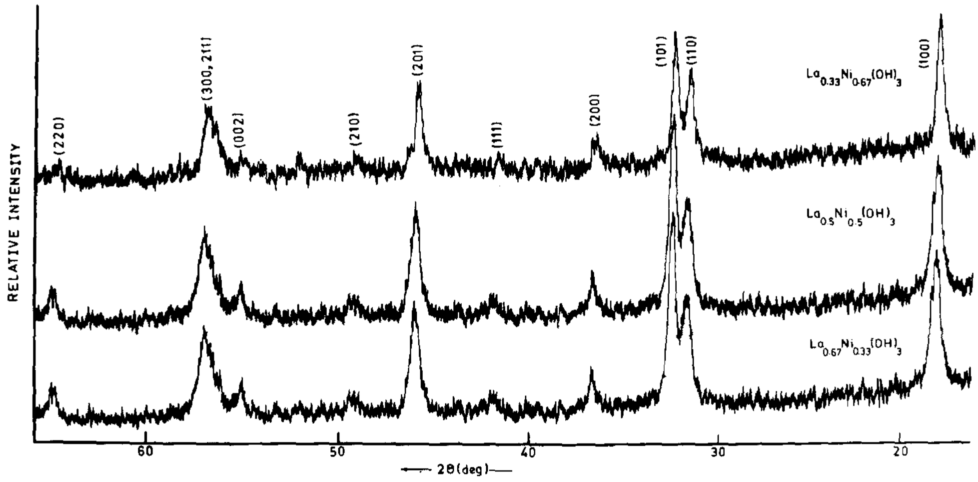

FIG. 2. X-ray powder diffraction patterns of $La_{1-x}Ni_x(OH)_3$ (λ = 1.7902 Å).

many perovskite oxides that cannot be obtained by the cyanide route (*3*) at temperatures lower than those normally required for their synthesis by the conventional ceramic method. For example, $LaNiO_3$ obtained by this method at 870 K has the composition $LaNiO_{2.97\pm0.02}$ with nearly 100% Ni^{3+}. $NdNiO_3$ was originally prepared by Demazeau *et al.* (*8*) by a high pressure method. We could synthesize this oxide by the hydroxide precursor route under ambient pressure at 870 K; the composition of

TABLE I

CRYSTALLOGRAPHIC DATA AND CONDITIONS FOR THE SYNTHESIS OF PEROVSKITE OXIDES FROM HYDROXIDE PRECURSORS

Hydroxide precursor	Lattice parameters (Å) a_h	c_h	Decomposition temperature (K)	Product oxide	Reaction conditions	Lattice parameters of the perovskite oxides (Å)
$La_{0.5}Al_{0.5}(OH)_3$	6.53	3.84	645	$LaAlO_3$	1220 K–12 hr–Air	Hexagonal, $a = 5.370$; $c = 6.550$
$La_{0.5}Cr_{0.5}(OH)_3$	X-ray amorphous		610	$LaCrO_3$	1120 K–12 hr–Air	Orthorhombic, $a = 5.575$; $b = 5.480$; $c = 7.753$
$La_{0.5}Fe_{0.5}(OH)_3$	6.53	3.84	660	$LaFeO_3$	1020 K–12 hr–Air	Pseudocubic, $a = 7.857$
$La_{0.5}Co_{0.5}(OH)_3$	6.53	3.84	630	$LaCoO_{2.98+0.02}$	1120 K–12 hr–O_2 atm	Hexagonal, $a = 5.500$; $c = 6.620$
$La_{0.5}Co_{0.25}Ni_{0.25}(OH)_3$	6.53	3.84	520–620	$LaCo_{0.5}Ni_{0.5}O_{2.97+0.02}$	1070 K–12 hr–O_2 atm	Hexagonal, $a = 5.548$; $c = 6.586$
$La_{0.5}Ni_{0.5}(OH)_3$	6.53	3.84	620	$LaNiO_{2.97\pm0.02}$	670 K–6 hr–O_2 atm	Hexagonal, $a = 5.525$; $c = 6.650$
$La_{0.5}Ni_{0.375}Cu_{0.125}(OH)_3$	6.53	3.84	620	$LaNi_{0.75}Cu_{0.25}O_{2.90\pm0.02}$	870 K–8 hr–O_2 atm	Pseudocubic, $a = 3.848$
$La_{0.5}Ni_{0.25}Cu_{0.25}(OH)_3$	6.53	3.84	670	$LaNi_{0.5}Cu_{0.5}O_{2.87\pm0.02}$	870 K–10 hr–O_2 atm	Pseudocubic, $a = 3.860$
$Nd_{0.5}Co_{0.5}(OH)_3$	6.42	3.74	630	$NdCoO_{2.98\pm0.02}$	970 K–12 hr–O_2 atm	Pseudotetragonal, $a = 5.340$; $c = 7.560$
$Nd_{0.5}Ni_{0.5}(OH)_3$	6.42	3.74	660	$NdNiO_{2.87\pm0.02}$	870 K–12 hr–O_2 atm	Pseudocubic, $a = 3.821$

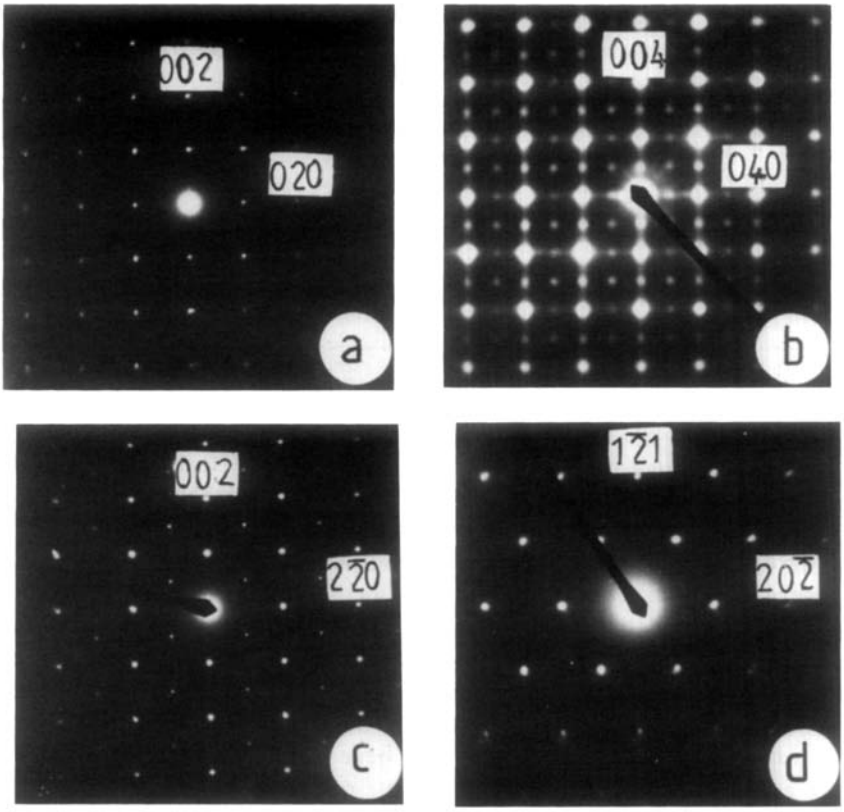

FIG. 3. Electron diffraction patterns of (a) $LaNiO_3$, [100]; (b) $NdNiO_{2.87\pm0.02}$, [100]; (c) $LaNi_{0.5}Cu_{0.5}O_{2.87\pm0.02}$, [110], and (d) $LaNi_{0.75}Cu_{0.25}O_{2.90\pm0.02}$, [111]. The electron beam directions are given within square brackets.

the oxide obtained by us is $NdNiO_{2.87\pm0.02}$.

We could not prepare $LaCuO_3$ by this method because the corresponding hydroxide precursor $La_{0.5}Cu_{0.5}(OH)_3$ cannot be made. We have, however, been able to prepare quaternary oxides of the type $La_{0.5}Ni_{0.5-x}Cu_xO_{1.5}$ by this method. Thermal decomposition of $La_{0.5}Ni_{0.375}Cu_{0.125}(OH)_3$ and $La_{0.5}Ni_{0.25}Cu_{0.25}(OH)_3$ (both crystallizing in the $La(OH)_3$ structure) in an oxygen atmosphere at 870 K yields the corresponding quaternary perovskite oxides. Chemical analysis of the oxidation states of the transition metals by the iodometric method shows that the compositions are respectively $LaNi_{0.75}Cu_{0.25}O_{2.90\pm0.02}$ (**I**) and $LaNi_{0.5}Cu_{0.5}O_{2.87\pm0.02}$ (**II**) indicating that Cu^{3+} is probably stabilized in these phases. Further evidence in support of the oxidation state of the transition metals was obtained by X-ray absorption spectroscopy (XAS) and XPS. Chemical shift of the Ni *K* absorption edge reported for Ni^{2+} oxides such as NiO and La_2NiO_4 is around 6.5 eV and the value for Ni^{3+} oxides such as $LaNiO_3$ and $Ba_2Ni_2O_5$ is around 10 eV (*9*). The chemical shifts of the Ni *K* edge in **I** and **II** were 9.7 ± 0.5 and 8.9 ± 0.5 eV, respectively, indicating that the oxidation state of Ni is close to 3+ in both these oxides. XPS of these oxides shows that the binding energy of $Cu(2p_{3/2})$ is 934.2 eV; the value is considerably higher than that observed for Cu^{2+} oxides such as CuO (933.2 eV) (*4*). The results indicate that nickel and part of copper are stabilized in the trivalent state in phases I and II. An-

TABLE II

CRYSTALLOGRAPHIC DATA OF CYANIDE SOLID SOLUTION PRECURSORS AND THE OXIDES OBTAINED FROM THEM

Cyanide precursor	Lattice parameters (Å)	Decomposition temperature (K)	Product oxide	Lattice parameters of the oxide (Å)
$La[Fe_{0.5}Co_{0.5}(CN)_6] \cdot 5H_2O$	$a_h = 7.546$; $c_h = 14.408$	620	$LaFe_{0.5}Co_{0.5}O_3$	$a_h = 5.484$; $c_h = 6.618$
$La_{0.5}Nd_{0.5}[Co(CN)_6] \cdot 5H_2O$	$a_h = 7.452$; $c_h = 14.299$	610	$La_{0.5}Nd_{0.5}CoO_3$	$a_0 = 5.396$; $b_0 = 5.356$; $c_0 = 7.600$

other quaternary oxide obtained by the thermal decomposition of the hydroxide precursor was $LaCo_{0.5}Ni_{0.5}O_3$ (Table I).

We have examined the electron diffraction patterns of **I** and **II** together with La NiO_3 and $NdNiO_{2.87\pm0.02}$ in order to find out whether there is any ordering of oxygen vacancies in $NdNiO_{2.87}$ and the two copper-containing oxides. $LaNiO_3$ (Fig. 3a) shows a typical cubic perovskite pattern in the [100] projection, while $NdNiO_{2.87}$ in the same projection (Fig. 3b) shows additional superlattice spots characteristic of the orthorhombic $GdFeO_3$ structure. Electron diffraction patterns of the perovskites **I** and **II** (Figs. 3c and d) recorded with the electron beam parallel to [100], [110], and [111] are similar to those of $LaNiO_3$; no evidence for anion vacancy ordering is seen from the electron diffraction patterns.

Cyanide Solid Solution Precursors

$LnM(CN)_6 \cdot 5H_2O$ (Ln = La, Ce, Pr, and Nd and M = Cr, Fe, and Co) are isostructural solids crystallizing in a hexagonal structure with the space group $P6_3/m$ (*10*). X-ray diffraction patterns showed that the two complex cyanides, $La[Fe_{0.5}Co_{0.5}(CN)_6] \cdot 5H_2O$ (**III**) and $La_{0.5}Nd_{0.5}[Co(CN)_6] \cdot 5H_2O$ (**IV**), prepared by us were single phases crystallizing in the same hexagonal structure with a = 7.546 and 7.452 Å and c = 14.408 and 14.299 Å, respectively. They decompose in air around 620 K. The products of decomposition obtained by heating **III** and **IV** in air at 670 K for 4 hr were poorly crystalline samples of the perovskite oxides $LaFe_{0.5}Co_{0.5}O_3$ (**V**) and $La_{0.5}Nd_{0.5}CoO_3$ (**VI**); higher temperatures (≥1020 K) were necessary to obtain crystalline samples of **V** and **VI**, which had the rhombohedral $LaCoO_3$ and orthorhombic Gd FeO_3 structures, respectively. Unit cell parameters of the cyanide solid solution precursors and the corresponding perovskite oxides are listed in Table II. These results show that it is indeed possible to prepare solid solution precursors $La_{1-x}Ln_xCo(CN)_6 \cdot 5H_2O$ (Ln = Nd etc.) as well as $LaFe_{1-x}Co_x(CN)_6 \cdot 5H_2O$ which on decomposition yield single-phase solid solutions of the perovskite oxides, $La_{1-x}Ln_x CoO_3$ and $LaFe_{1-x}Co_xO_3$. It has been found from our experience that preparation of such quaternary perovskite oxides by the ceramic method is tedious and often impossible; the cyanide solid solution method affords a convenient route for the synthesis of such homogeneous samples of quaternary perovskite oxides.

Nitrate Solid Solution Precursors

It is known that anhydrous alkaline earth metal nitrates, $A(NO_3)_2$ (A = Ca, Sr, Ba), and $Pb(NO_3)_2$ and $Cd(NO_3)_2$ are isostructural, crystallizing in the cubic structure with the space group $P2_13$ (*11*). We have prepared the solid solutions $Ba_{1-x}Pb_x(NO_3)_2$ (x = 0.33, 0.40, 0.50, 0.67), $Sr_{1-x}Pb_x(NO_3)_2$ (x = 0.33 and 0.50), and

TABLE III

CRYSTALLOGRAPHIC DATA AND CONDITIONS FOR THE SYNTHESIS OF METAL OXIDES FROM NITRATE PRECURSORS

No.	Nitrate precursor	Cubic unit cell parameter (Å)	Product oxide	Reaction conditions	Lattice parameters of oxides (Å)
1	$Ba(NO_3)_2$	8.118	—		
2	$Ba_2Pb(NO_3)_6$	8.024	Ba_2PbO_4	1270 K—12 hr—Air	$a = 4.305$; $c = 13.273$
3	$Ba_3Pb_2(NO_3)_{10}$	8.015	—		
4	$BaPb(NO_3)_4$	7.992	$BaPbO_3$	970 K—4 hr—Air	$a = 4.270$
5	$BaPb_2(NO_3)_6$	7.945	—		
6	$Pb(NO_3)_2$	7.857	—		
7	$SrPb(NO_3)_4$	7.824	$SrPbO_3$	1070 K—12 hr—Air	$a = 5.860$; $b = 5.950$; $c = 8.325$
8	$Sr_2Pb(NO_3)_6$	7.808	Sr_2PbO_4	1170 K—12 hr—Air	$a = 6.612$; $b = 10.080$; $c = 3.505$
9	$Sr(NO_3)_2$	7.781	—		
10	$BaSrPb(NO_3)_6$	7.940	$BaSrPbO_4$	1220 K—12 hr—Air	$a = 4.280$; $c = 12.842$

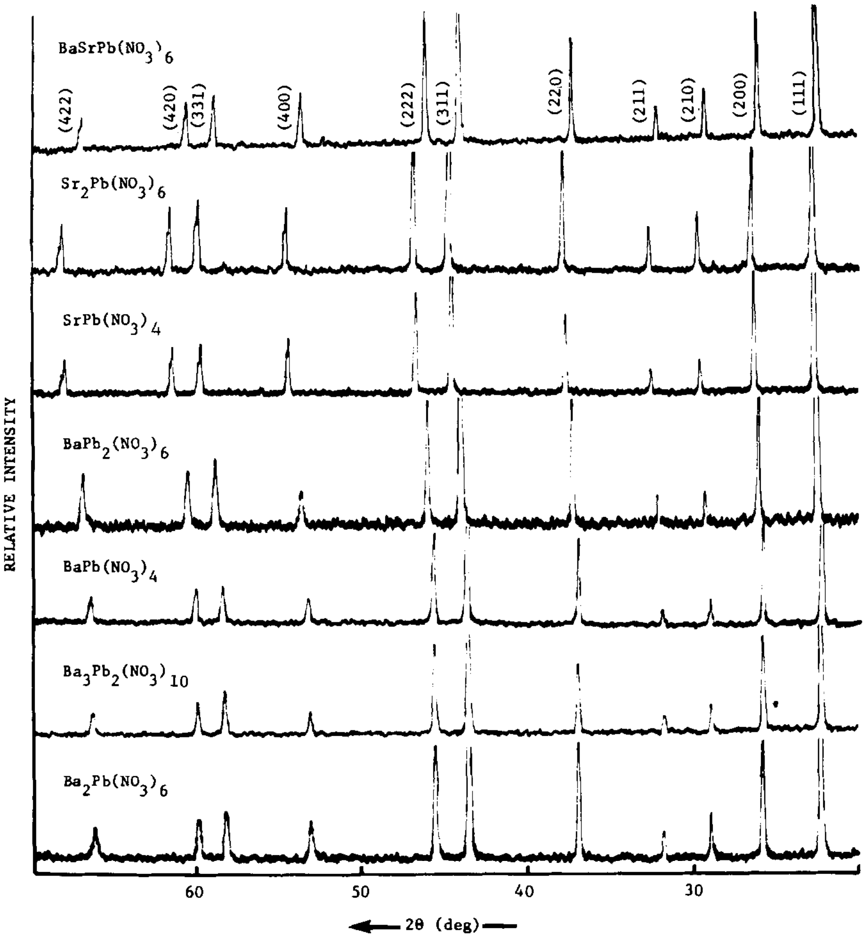

FIG. 4. X-ray powder diffraction patterns of nitrate solid solutions ($\lambda = 1.7902$ Å).

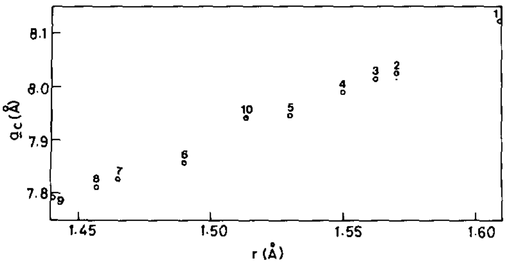

FIG. 5. Plot of cubic unit cell parameter, a_c, of the nitrate solid solutions versus weighted mean cation radius, r. The numbers refer to the compositions given in Table III.

$Ba_{1-x-y}Sr_xPb_y(NO_3)_2$ ($x = y = 0.33$) crystallizing in the cubic $Ba(NO_3)_2$ structure (*12*). The compositions of the nitrate solid solutions together with their cubic cell parameters are listed in Table III. X-ray powder diffraction patterns of the nitrate solid solutions (Fig. 4) indeed show remarkable similarity and the cubic lattice parameters (*13*) of the nitrate solid solutions increase linearly with the increase in weighted mean radius (*14*) of the cation in 12-coordination as shown in Fig. 5. The slope and intercept of the straight line are 1.91 and 5.01, respectively, and the correlation coefficient is 0.90. Infrared spectra of the nitrate solid solutions are typical of the $Ba(NO_3)_2$ structure showing absorption bands around 1380, 1060, 820, and 720 cm^{-1} due to ν_3, ν_1, ν_2 and, ν_4 modes, respectively, of the nitrate ion (*15*).

The nitrate solid solutions decompose at temperatures intermediate between the decomposition temperatures of the end members. For example, $BaPb(NO_3)_4$ decomposes endothermally at 770 K, while $Ba(NO_3)_2$ and $Pb(NO_3)_2$ decompose at 860 K and 750 K, respectively (*16*). $BaPb(NO_3)_4$ decomposes endothermally into a mixture of binary oxides at 770 K which on further heating yields single phase $BaPbO_3$ around 820 K as revealed by DTA and XRD. Stoichiometric $BaPbO_3$ (Fig. 6) can best be prepared by heating the nitrate precursor at 970 K for 4 hr in air in a preheated furnace. $BaPbO_3$ has been prepared in the literature (*17*) by the reaction of $BaCO_3$ and Pb_3O_4 at 1250 K. The method suffers from several disadvantages which include the loss of

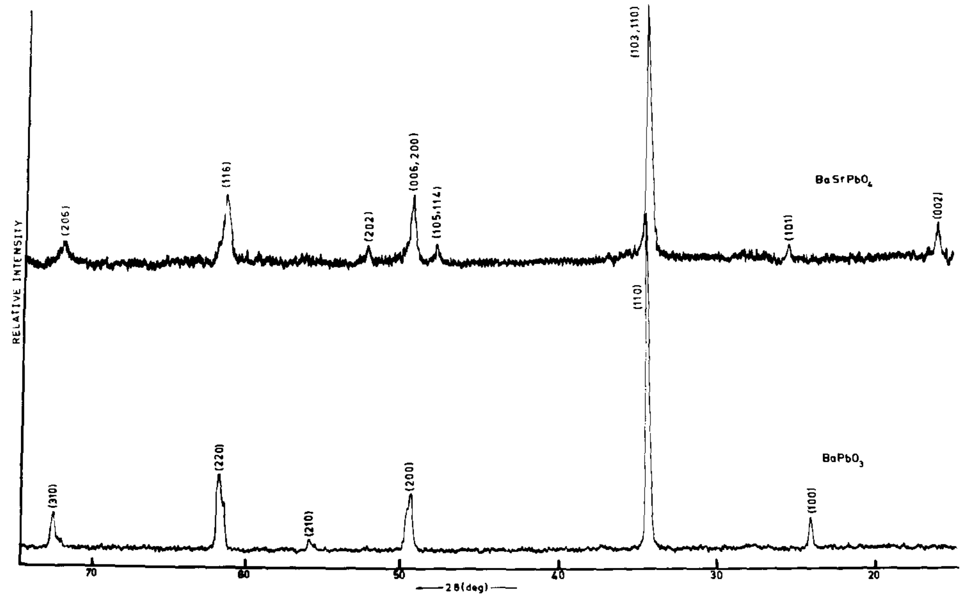

FIG. 6. X-ray powder diffraction patterns of $BaPbO_3$ and $BaSrPbO_4$ ($\lambda = 1.7902$ Å).

PbO at high temperatures resulting in nonstoichiometry (*18*). The nitrate precursor route is simple and straightforward yielding the stoichiometric product at a considerably lower temperature, thus avoiding the volatilization of lead oxide.

Compositions of other oxides obtained from nitrate precursors, together with the conditions for formation and structural details, are listed in Table III. Ba_2PbO_4 crystallizing in the perovskite-related K_2NiF_4 structure (*19*) could be prepared by heating its precursor in air at 1270 K for 6 hr. Attempts to prepare other members of the $AX(ABX_3)_n$ series such as $Ba_3Pb_2O_7$ were unsuccessful. Sr_2PbO_4 and $SrPbO_3$ could be prepared from the nitrate precursors and their X-ray diffraction patterns agree well with those reported in the literature (*20, 21*). The nitrate solid solution precursor method has enabled us to synthesize a new oxide, $BaSrPbO_4$, crystallizing in the K_2NiF_4 structure with $a = 4.280$ and $c = 12.842$ Å. The compound is formed by heating $BaSrPb(NO_3)_6$ at 1270 K for 10 hr in air. $BaSrPbO_4$ which can be regarded as 1 : 1 solid solution of Ba_2PbO_4 and Sr_2PbO_4 adopts the Ba_2PbO_4 structure rather than the Sr_2PbO_4 structure (Fig. 6). The X-ray powder diffraction pattern does not indicate an ordering of the Ba and the Sr atoms.

Acknowledgments

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