Articles

Synthesis of $La_{1-x}Sr_xCoO_3$ ($x \leq 0.2$) at Low Temperature from PVA-polymeric Gel Precursors

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Single phase $La_{1-x}Sr_xCoO_3$ ($x \leq 0.2$) was synthesized as a uniform sized 100 nm particulates with relatively high surface area of 20-30 m^2/g, at low temperature (≥ 600 °C), from a polymeric gel precursors prepared by using poly(vinyl alcohol) as homogenizer. No minor phase developed during the crystallization when polymer/metal mole ratio was higher than 3. As the polymer/metal mole ratio was raised in the gel, the amount of carbonaceous residues in the amorphous solid precursor prepared by heating the gel at 300 °C increased. Most of the residues were eliminated by exothermic thermal decomposition around 400 °C. The amount of residual carbon (less than 1%) left in the crystalline $La_{1-x}Sr_xCoO_3$ decreased as more polymer was used, eliminating detrimental effect which might be posed by using large amount of organic homogenizer. The crystal structure of $La_{1-x}Sr_xCoO_3$ synthesized at temperature lower than 800 °C was observed to be shifted from rhombohedral to more symmetric cubic. The structure shifted back to rhombohedral as the cubic sample was annealed at 1000 °C.

Introduction

Mixed metal oxides with perovskite structure (ABO_3) have interesting properties which render the material be attractive for their possible applications, such as catalysts in hydrogenation and oxidation[1-3] or as high temperature fuel cell electrodes.[4-6] Especially, $La_{1-x}Sr_xCoO_3$ ($LaCoO_3$ doped with Sr) exhibited a good catalytic reactivity,[7] and had high conductivity at elevated temperature.[8]

$LaCoO_3$ belongs to the space group of R3c, and has a rhombohedral crystal structure with a=0.5436 nm and α= 60°48'.[9] As $LaCoO_3$ was doped with Sr, it was observed that the catalytic reactivity and the conductivity were both largely enhanced.[7,8] Keeping compositional homogeneity in $La_{1-x}Sr_xCoO_3$ was suggested to be imperative for getting such enhancements.[10] Also, maximizing surface area of the material was beneficial for applying it as a catalyst.[11]

Conventionally, perovskite-type mixed metal oxides were synthesized *via* solid state reaction by heating constituent metal carbonates, or sometimes precipitates (coprecipitation) of constituent metal acetates or nitrates.[7,12-15] The method required heating of the solid reactants at high temperature (usually higher than 1000 °C) during elongated time, sometimes with intermittent cooling and grindings. Often, the product was laced with compositional inhomogeneity and minor phases. To achieve homogeneity of the composition, and enhance surface area of the sample at the same time, several variations of unconventional methods were adopted. By citrate method, perovskites such as $(La,Sr)MnO_3$, $(La,Ca)MnO_3$, $(La,Ca)CoO_3$, $La(Mn,Cu)O_3$, $La(Co,Fe)O_3$, and $La(Co,Cu)O_3$ were synthesized as a single phase crystalline

powder around 600 °C.[10,11,16] But, the method was not effective in producing single phase $(La,Sr)CoO_3$, and only generated a mixture of minor phases. Preparation of single phase $(La,Sr)CoO_3$ by the method required heating at 1060 °C to remove the minor phases,[16] which provided not much benefit over the solid state reaction. For the synthesis of some perovskite-type mixed metal oxides, a few organic polymers were also used as homogenizer in order to prevent the generation of minor phases during the synthesis. For example, $La_{1-x}Sr_xFe_{1-y}Co_yO_3$ was synthesized from polymeric precursor prepared by using poly(ethylene glycol).[17] $LaCoO_3$ and $(La,Sr)MnO_3$ were also synthesized from polymeric precursors prepared by use of poly(acrylic acid).[18-21]

In this study, single phase crystalline $(La,Sr)CoO_3$ was synthesized *via* polymeric precursors prepared by using poly(vinyl alcohol) as homogenizer. Poly(vinyl alcohol) is water soluble and has hydroxy ligands as side groups which provide complexing sites to metal ions. By the method, $(La,Sr)CoO_3$ could be synthesized at 600 °C as a single phase crystalline powder which had uniform particle size and high surface area. The first use of PVA in synthesizing perovskite mixed metal oxides was previously reported by us elsewhere.[22,23] Recently, the syntheses of several mixed metal oxides, such as PZT and PLZT, by using PVA were also reported by others.[24]

Experimental

Synthesis. Strontium nitrate, $Sr(NO_3)_2$, and cobalt nitrate hexahydrate, $Co(NO_3)_2 \cdot 6H_2O$, were both purchased from Junsei Co., Japan. Lanthanum nitrate hexahydrate, $La(NO_3)_3 \cdot 6H_2O$, was purchased from Yakuri Pure Chemicals Co., Japan. Poly(vinyl alcohol), PVA, was purchased from

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Junsei Co., Japan. The degree of polymerization of the PVA was 1500. All the chemicals were reagent grade.

Metal components of the polymeric precursors were provided from constituent metal nitrates. In a 500 mL beaker, La(NO₃)₃·6H₂O (4.36 g), Sr(NO₃)₂ (6.53 g) and Co(NO₃)₂·6H₂O (3.67 g) were dissolved in 200 mL of deionized distilled water. In another beaker, 6.80 g of PVA (PVA/metal mole ratio=6) was dissolved in 200 mL of lukewarm deionized distilled water with mechanical stirring. While the mixture was magnetically stirred, the metal nitrate solution was well mixed with the PVA solution, which generated a pink transparent solution mixture. To remove water, the mixture was heated at 70-80 °C while it was mechanically stirred. As water evaporated, the solution turned into a very viscous gel. For the preparation of the gel (polymeric precursor) with different PVA/metal mole ratios, or with different La to Sr mole ratios, the same procedure was followed, except the amount of reactants used. PVA to metal ratio was 0, 1, 3, 6, or 10. The La to Sr mole ratio was varied from 1 : 0 to 0.4 : 0.6. For the comparison study, coprecipitation precursor (PVA/metal ratio of 0) was also prepared by boiling a solution of constituent metal nitrates down to a dry. The gels were reduced into dark brown powders by being heated at 300 °C for 1 h. The powders were further heated at 800 °C to acquire about 3 g of single phase polycrystalline La₁₋ₓSrₓCoO₃ (which will be refered as LSCO).

Characterization. Powder X-ray diffraction (PXRD) pattern of the sample was obtained with Rigaku D-MAX 2000 diffractometer and Siemens model D-500 using CuK radiation. Thermogravimetric analysis (TGA) was done by the use of TGA-1000 from Stanton Redcroft Co. Differential Scanning Calorimetry (DSC) was carried out with DSC-1500 from Stanton Redcroft Co. FTIR spectra were taken from KBr pellets by using MB-102 from Bomem. Elemental analysis was carried out by combustion method. Surface area of the sample was measured with Quantachrome Autosorbe by multi-point BET method using N₂ gas. SEM pictures were taken with Hitachi S-4100, and microprobe elemental analysis was performed by TN-voyager.

The gels were heated to 1000 °C at 10 °C/min in the flow of air, and their pyrolyses were studied by DSC and TGA. The same was done for sole PVA, to see the effect of constituent metal nitrates on the pyrolysis of the gel. The gel was heated at various temperatures (300, 500, 600, and 800 °C) in an ambient atmosphere, and resultant powders were characterized by PXRD and FTIR. The same heating procedure was used for the gels synthesized from reactants of various different stoichiometries.

Results and Discussion

Synthesis. Any compositional heterogeneity developed in the precursor would result in a formation of undesirable minor phases upon the precursor being heated. Most of all, differentiated precipitation, which may occur while solution precursor transformed into solid precursor, is detrimental to the attainment of compositional homogeneity. In order to oppress the differentiated precipitation during removal of solvent from the solution of constituent metal nitrates, PVA was used as homogenizer. The synthesis of the polycrystalline LSCO *via* polymeric gel precursor was schemat-

ically shown in Figure 1. Upon removal of water by heating the pink solution mixture around 80 °C, the solution turned into a very viscous transparent pink-colored gel. The clearness of the gel indicated that the composition of the gel was homogeneous. Water could not be removed completely from the gel within reasonable time, leaving about 10% water in the gel (assessed by TGA). When the viscous gel was pre-treated at 300 °C, it turned into dark brown powder. The powder was very fine and fluffy. As the powder was further heated above 400 °C, it turned black.

Pyrolysis. The pyrolysis of the gel-precursor was monitored by thermal analyses and compared to the one for sole PVA in Figure 2 and 3. Unless specified, PVA/metal mole ratio of 6 and stoichiometric unit x of 0.2 in La₁₋ₓSrₓCoO₃ was chosen as a representative composition of the gel. Whereas several indiscrete weight decreases continued up to 630 °C (accompanying exotherms in the DSC trace) for sole PVA (Figure 2-a and 3-a), for the pyrolysis of the gel, the weight decrease terminated around 400 °C, and three discrete weight losses were observed around 80, 230, and 400 °C (Figure 2-b). The weight loss around 80 °C, which accompanied an endotherm in Figure 3-b, corresponded to the removal of residual water. The weight losses at 230 and 400 °C accompanied exotherms, which indicated that the organic moieties in the gel decomposed *via* two consecutive steps. The first step pyrolysis appeared to be catalytically fueled by metal nitrates by seeing that the dried gel was self burning if once ignited. At this step, nitrates acted as an oxidizer,[24] and it was presumably propped up by catalytic role of the metal ions, burning the organic components in the gel at low temperature. This burning of the gel around 230 °C accompanied violent gas evolution, which made the resultant powder be fluffy and fine. The produced gases were presumed to be NO₂ and CO₂, by considering same kind of gases had been observed by mass spectrometry
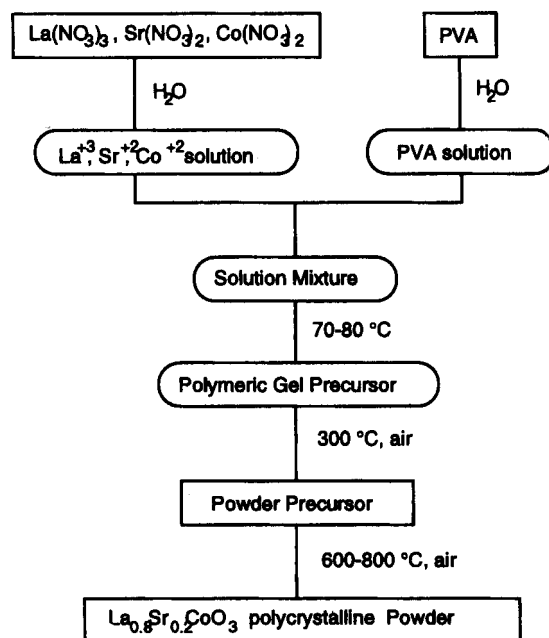
**Figure 1.** Schematic outline of the preparation of polycrystalline La₁₋ₓSrₓCoO₃ ($x \leq 0.2$). Water soluble organic polymer, poly(vinyl alcohol), was used as homogenizer.

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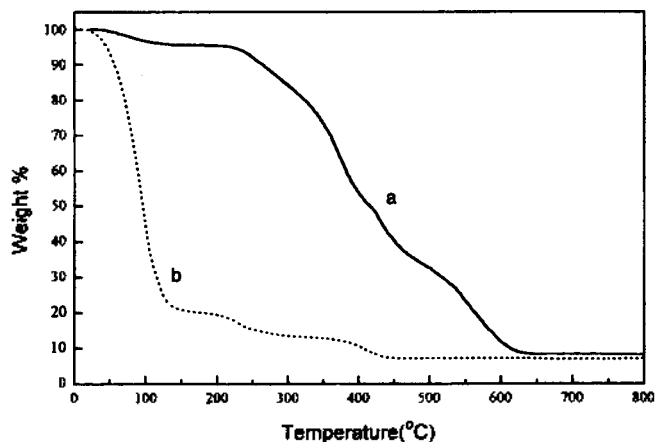
Figure 2. TG traces for the pyrolysis of: a) sole PVA without being mixed with the metal ions; b) polymeric gel precursor prepared from the mixture of aqueous solutions of PVA and metal nitrates.

upon decomposition (around 200 °C) of gel precursors prepared *via* citrate process.[10]

On assessing the data from TG and elemental analyses, it was suggested that the oxidation of the organic components in the gel at 230 °C was incomplete. About half amount (by TG) of initial PVA moieties remained in the precursor, supposedly as carbonaceous residues, after they pyrolyzed around 230 °C (first step pyrolysis). These residues decomposed in subsequent second step pyrolysis around 400 °C. Compared to the extent of the weight loss, the size of the exotherm at 400 °C was relatively big, which indicated that the residues burned into oxidized form (CO or CO$_2$). This heat event at 400 °C was observed whether the precursor was pretreated at 300 °C or not (Figure 3-c vs 3-b), which excluded the possible involvement of nitrates at the temperature. The role of some transition metals and metal oxides as combustion catalysts is known.[25,26] Therefore, it was suggested that the metal ions which were homogeneously distributed through the media catalytically enhanced the decomposition of the organic residues, thereby, lowering the
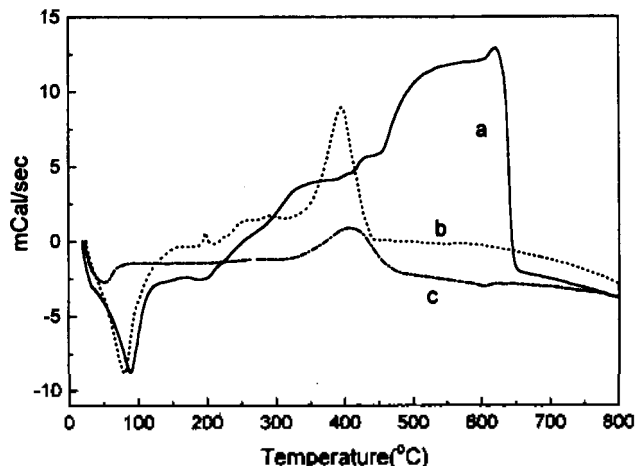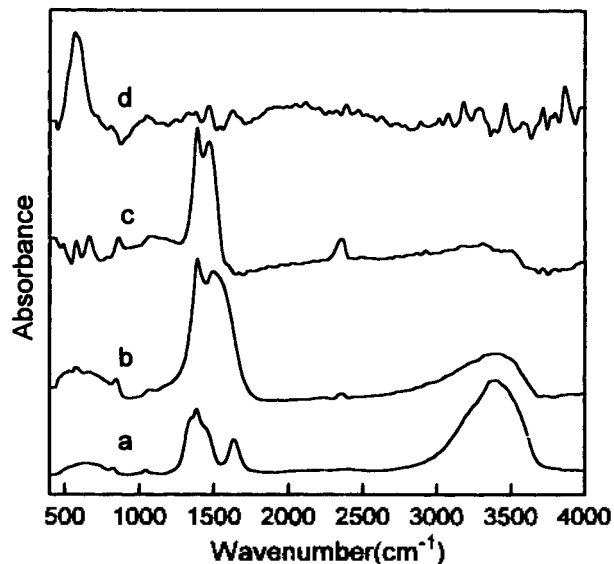
temperature of complete decomposition of PVA from 650 to 400 °C. With both diffusion barrier and carbonaceous residues eliminated, the crystallization at low temperature became possible.

FTIR spectra taken from the powder samples prepared by heating the polymeric gel precursors at 120, 300, 500, and 800 °C were shown in Figure 4. Upon being heated at 300 °C, the peaks around 1300, 1400, and 1650 cm^{-1} disappeared, and the peaks around 1350, 1450, and a shoulder at 1550 cm^{-1} developed. This observation suggested that the PVA moieties were destroyed and resultant carbonaceous residues were left in the precursor, one of which should be carbonate.[27-29] When the precursor was further heated at 500 °C, the carbonate peaks persisted (the relative intensity largely diminished, but shown magnified in the figure for comparison) and the shoulder disappeared. Therefore, it was suggested that large fraction of the residues in elemental or cluster form was eliminated during decomposition at 400 °C. Previous study on citrate process by others also pointed out that nitrates decomposed prior to the combustion of the citrate.[10] Upon crystallization above 600 °C, metal-oxygen vibration was observed around 600 cm^{-1}.

Crystallization. The PXRD patterns in Figure 5 showed the crystallization of the precursor into a single phase crystalline LSCO around 600 °C. The powder heated at 500 °C showed only a broad peak which is typical for the amorphous powder. The powder became crystalline after 600 °C, showing major diffractions of LSCO at 23.2, 32.8, 33.1, and 47.5°(2θ).[30] The precursor crystallized into a single phase LSCO without any development of minor phase, when Sr/La mole ratio was lower than 0.2/0.8. It took less than an hour to attain full crystallinity. When the Sr/La mole ratio of the precursor was higher than 0.3/0.7, undesirable minor phases developed upon being heated. In solid state reaction which utilized metal carbonates, the reactants started forming initial crystalline perovskite at 850 °C, and it took elongated time to attain desired phase, after sev-

Figure 3. DSC curves for the pyrolysis of: a) sole PVA; b) the polymeric gel precursor to La$_{0.8}$Sr$_{0.2}$CoO$_3$; c) the powdery precursor obtained by heating the gel at 300 °C prior to the DSC measurement.


Figure 4. FTIR spectra taken from the powder samples prepared by heating the gel precursor in air at: a) 120 °C for 12h; b) 300 °C for 1h; c) 500 °C for 1h; d) at 800 °C for 1h.
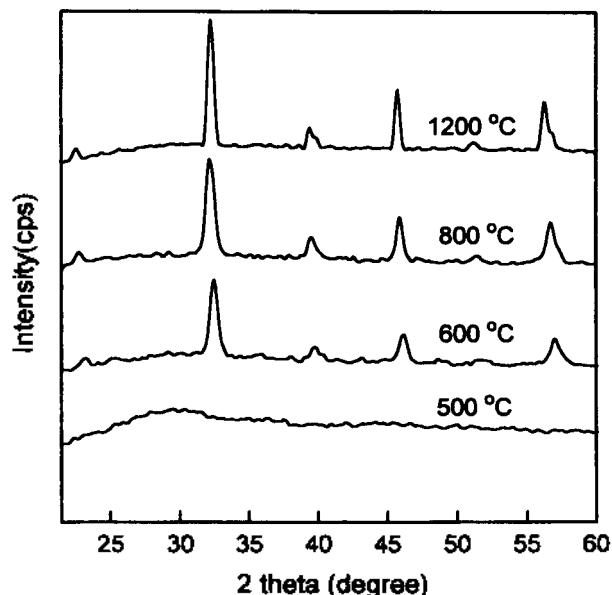
Figure 5. PXRD patterns of the powder samples prepared by heating the precursor at designated temperatures for 1h.

eral intermittent cooling and grinding steps which were detrimental to the quality of the final products. This tedious procedure was required in order to overcome diffusion barrier which was existent among any heterogeneous domains in the sample. The use of PVA as homogenizer suppressed the formation of such heterogeneous domains by oppressing the differentiated precipitation while the gel decomposed into the solid precursor. By preserving the compositional homogeneity in the precursor, the diffusion barrier was eliminated.[24] It was presumed that the hydroxy ligands on PVA interacted with (or were complexed to) the metal ions, and wrapped into a cocoon-like structure around the ions, such as the one suggested in Figure 6. The chemical interaction similar to the one shown in the figure was proposed by others for the syntheses of metal oxides which utilized poly(acrylic acid) as homogenizer.[31] This local isolation would prevent agglomeration of metal components, cutting off the proceeding toward the formation of pre-
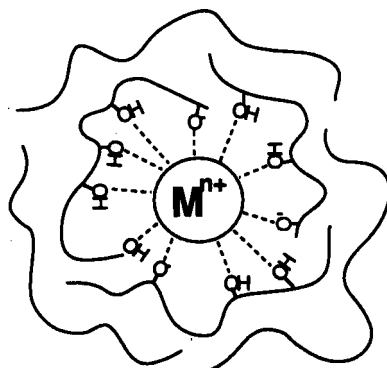
Figure 6. Proposed example of cocoon-like local structure around metal ions formed by the interaction of hydroxide side groups on the PVA with the metal cation. The curved lines denote the backbone of the poly(vinyl alcohol) polymer chains which are sided with the hydroxyl groups.

cipitates. This isolation would be preserved until the organic moieties burned off by being heated.

PXRD peaks of the LSCO appeared rather broad, reflecting small size of the crystallites. The size of the crystallites calculated by Scherrer's equation[32] from the half peak width of LSCO (012) peak (at $2\theta=23.05°$) and silicon (111) peak (at $2\theta=28.30°$) was 20 nm. For the practical application of the material as the cathode in a fuel cell, the size of the crystallites (conversely, the area of grain boundary, and the ratio of surfacial atoms to bulk ones) should be one of major factors which would greatly influence the magnetic, electrical, and mechanical properties of the material.
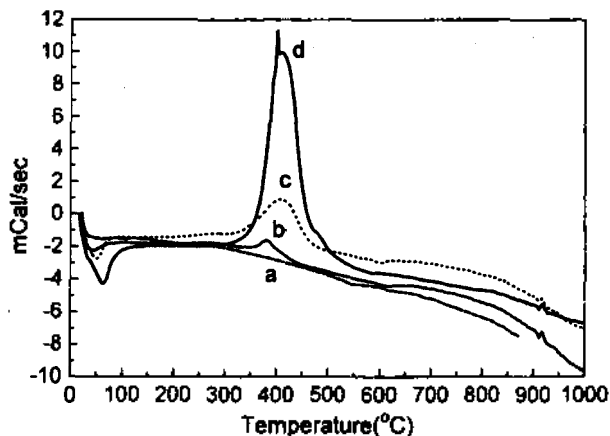
The stoichiometric effect of PVA on the carbon residues. The use of PVA enhanced the processability of the material by achieving the homogeneity of the media. But, as mentioned in other's study,[16] the decomposition of organic moieties in the precursor unavoidably left carbonaceous residues in the product. Table 1 presents carbon contents in the precursors prepared by heating the gels with different PVA/metal mole ratios at 300 °C, and in the crystalline products attained by heating the precursors at 800 °C. As more PVA was used in preparing the gel, more carbonaceous residues were present in the precursor heated at 300 °C. On the contrary, the trend in the carbon contents in the crystalline powder after being heated at 800 °C became opposite to the one in the previous one; as more PVA was used for the gel, less carbon residue was present in the crystalline product. These rather contradictory trends, especially the one for the crystalline products,[33] may be useful in tailoring the amount of carbon which can be intentionally (and homogeneously) added to crystalline perovskite. Most of all, this opposite trend would enable one to use fairly large amount of PVA without posing the limitation stemmed from the deteriorating effect of carbon remnants in the sample.

The exact chemical and physical form of the carbonaceous residues cannot be known. From the FTIR observation (see above) it was speculated that some of the residues could be carbonates. But, by considering the TG weight loss between 400 and 800 °C was negligible (whereas FTIR peaks disappeared) the major constituents were not carbonates, but possibly in cluster form. From the fact that the gel precursor had high degree of homogeneity, it was assumed that the distribution of these carbon species was homogeneous, too.

Figure 7 showed DSC traces during the pyrolysis of the precursors prepared from the gels with different PVA to metal mole ratios. Major difference among the traces was the

Table 1. Carbon contents in the samples prepared by heating various gel precursors with different PVA/Metal mole ratios at the designated temperatures for 1h

PVA : metal (processing temp)	Carbon content (weight %)
1 : 1 (300 °C)	1.97
3 : 1 (300 °C)	4.10
6 : 1 (300 °C)	10.09
1 : 1 (600 °C)	0.83
3 : 1 (600 °C)	0.31
6 : 1 (600 °C)	0.25

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Figure 7. DSC traces for the pyrolysis of the precursors with various different PVA/metal mole ratios. The PVA to metal mole ratios were a) 1 : 1, b) 3 : 1, c) 6 : 1, and d) 10 : 1.

size of the exotherm around 400 °C. The size of the peak appeared roughly proportional to the amount of carbonaceous residues left in the precursors (see table 1). Therefore, it appeared that most of the residues decomposed around 400 °C, generating gaseous products. It is speculated that CO_2 gas produced at this second step combustion further reacted with remaining residue. Around 950 °C, same kind of reaction between CO_2 and free carbon in $SrMnO_3$ prepared from gel precursor is known to occur.[10] Therefore, the decomposition of carbonaceous residues (around 400 °C) took extra free carbon by the reaction between CO_2 and C, lowering the carbon content of the sample further than expected, which resulted in the reversed trend of the carbon contents in the crystalline samples.

The stoichiometric effect of PVA on the crystal structure. Figure 8 shows the stoichiometric effect of PVA on the crystallization of the precursor, observed by PXRD. The precursor prepared with no PVA addition corresponds to the one made by coprecipitation method. In the case, the compositional inhomogeneity caused by the formation of precipitates encouraged the development of undesirable minor phases. The crystalline product from this
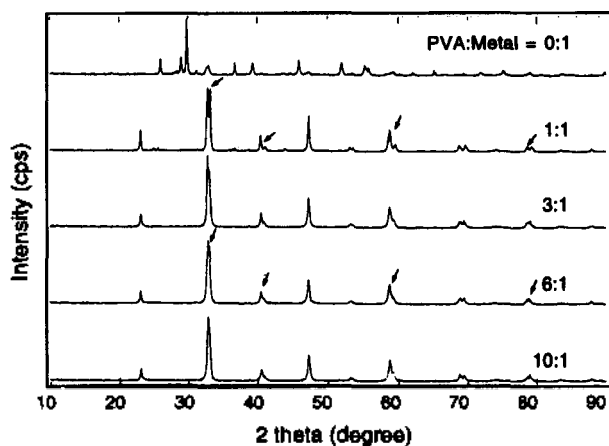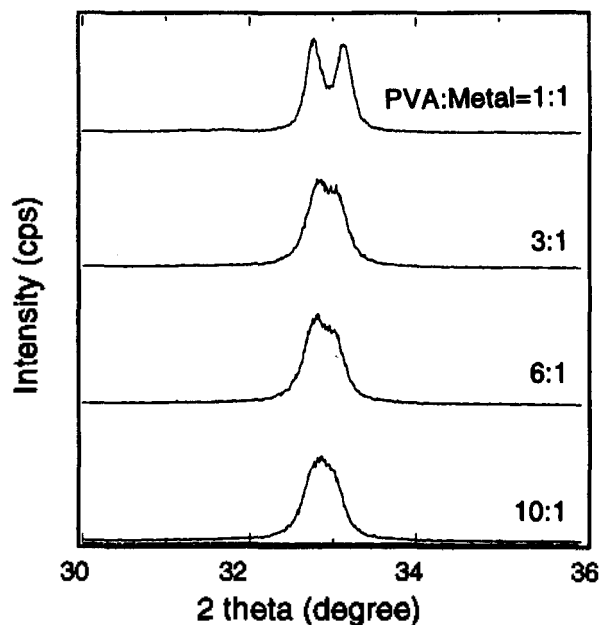
coprecipitated precursor was a mixture of several phases; La_2O_3, Co_3O_4, and $La_{1-x}Sr_xCoO_3$ with a range of x. On the contrary, the use of PVA greatly suppressed the formation of minor phases by enhancing the homogeneity of the media.[24] The diffusion barrier among heterogeneous domains would be eliminated. Without the diffusion barrier, the precursor crystallized directly into desired LSCO at low temperature.

The increase of Sr content in the LSCO is known to shift the crystal structure toward higher symmetry; as some La is replaced by Sr, the rhombohedral crystal structure of LSCO transforms to cubic. By the effect, several sets of twin peaks on the PXRD patterns of $La_{1-x}Sr_xCoO_3$ were observed to merge as x increased.[30] The difference between 2θ values of two major diffractions, (110) and (104), of $La_{1-x}Sr_xCoO_3$ was 0.376, 0.201, and 0.000 for x=0.1, 0.4, and 0.5, respectively.[30] It could be seen that the two peaks merged together as Sr content increased. In our study, the same kind of structural shift was observed just by changing the PVA stoichiometry in the gel, even though the Sr content was kept constant. The merge of the two peaks was apparent in Figure 9 which showed slow scans on (110) and (104) diffractions. As the PVA/metal mole ratio increased in the gel, those two diffractions appeared further to be merged, which indicated the crystal structure became more symmetric. When these samples were further annealed at 1000 °C in air, this structural shift was reversed, and all had same rhombohedral structures whose the PXRD patterns were shown in Figure 10.

One possible cause for this structural shift might be the inclusion of carbon species in the crystal lattice. The structural change caused by carbon residue was reported for some superconducting mixed metal oxides doped with carbon in carbonate form.[34,35] The structural shift was also ob-

Figure 8. PXRD patterns of $La_{0.8}Sr_{0.2}CoO_3$ synthesized by heating gel precursors with various different PVA/metal mole ratios at 800 °C.

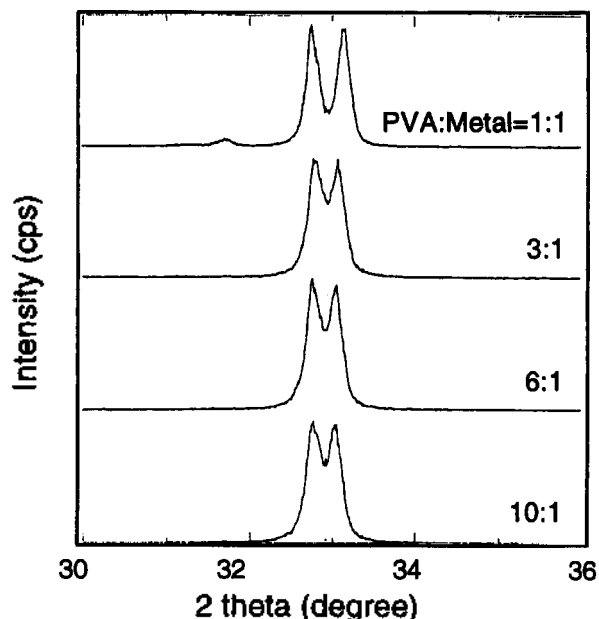**Figure 9.** PXRD patterns of $La_{0.8}Sr_{0.2}CoO_3$ synthesized by heating gel precursors with various different PVA/metal mole ratios at 800 °C. Only (110) and (104) diffractions were obtained with slow scan rate.

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Figure 10. PXRD patterns of $La_{0.8}Sr_{0.2}CoO_3$ prepared by annealing the samples used for taking the PXRD patterns in the Figure 9, at 1000 °C for 1h in air. Only (110) and (104) diffractions were obtained with slow scan rate.

Figure 11. SEM images of powders prepared by heating the gel precursors at: a) 400 °C for 1h (magnification of 2000); b) 800 °C for 1h (magnification of 30000).

served in olivine $((Mg_{2-x}Fe_x)SiO_4)$ minerals doped with carbon.[36] But, by considering the carbon content was very low, and the extent of the structural change was minute, the inclusion of carbon species is not plausible. The structural change could also be caused by stoichiometric deficiency of the lattice oxygen. For the crystalline $LaMnO_3$ synthesized from poly(acrylic acid) gel, the similar effect was observed.[18] As more poly(acrylic acid) was used, the crystal structure of $LaMnO_3$ shifted from hexagonal to orthorhombic, and the shift was also reversed by further annealing at higher temperature. In that study, the oxygen content was related to the structural shift; as more poly(acrylic acid) was used in the gel, more oxygen deficiency was observed in the crystalline product which presumed to cause the structural shift. It is speculated that the same kind of oxygen deficiency caused the structural shift in the LSCO. As pointed out in the previous section, larger amount of carbonaceous residues were present in the precursor, as more PVA was used in the gel (see Table 1). Upon being heated above 400 °C, this carbonaceous residues generated CO_2 gas, some of which presumed to react further with elemental carbon, generating CO.[10] As more PVA was present in the gel, larger amount of CO_2 and CO will be generated around sample, which should locally provide highly reducing environment. Thereby, oxygen deficiency occurred while the precursor crystallized, which caused the structural shift.

Morphology. Figure 11 shows the morphology of the precursors after heat treatment at specified temperatures. The fluffy powder generated by heating the gel at 400 °C had irregular shape which resembled crumbled thin paper. When the fluffy powder was further heated at 800 °C, turning it into crystalline LSCO, the morphology of the sample changed into a collection of particles. The size distribution was fairly narrow and the average diameter of the particle was 100 nm. The elemental analysis by microprobe (EDX)
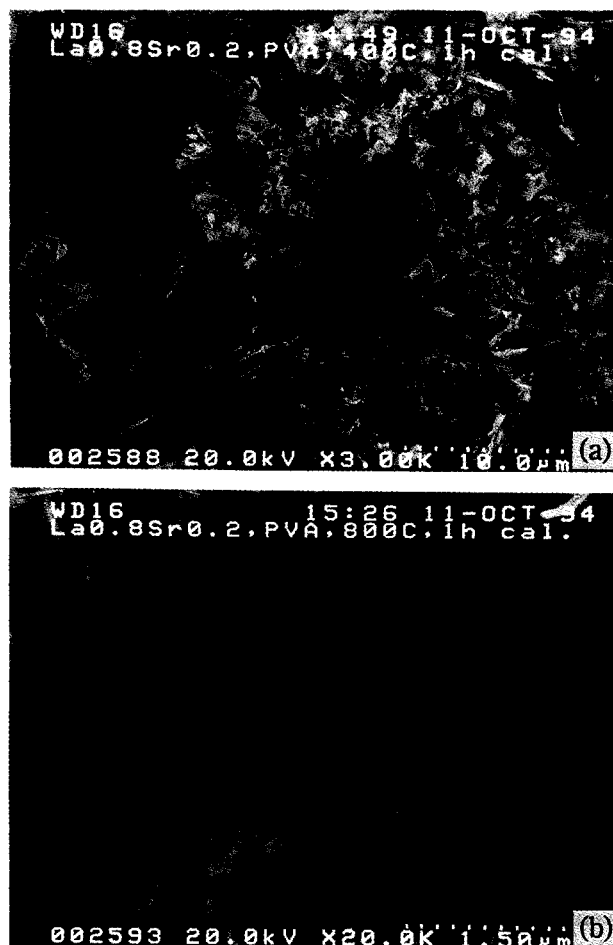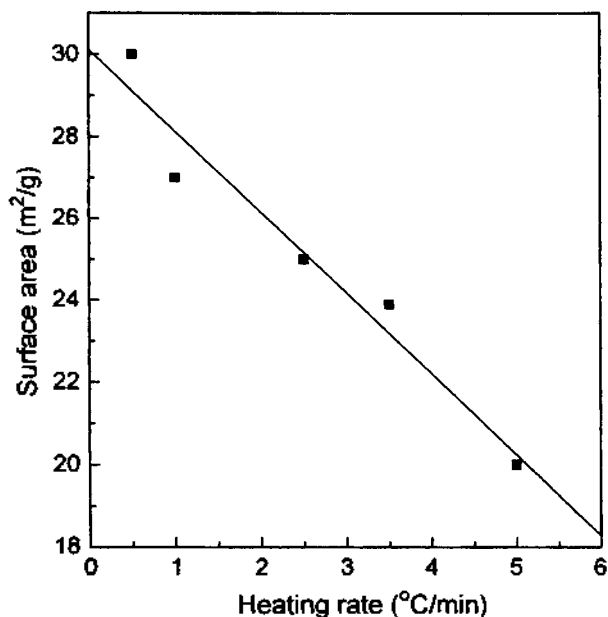
Figure 12. The dependence of the BET surface area of the crystalline $La_{0.8}Sr_{0.2}CoO_3$ upon the heating rate. The heating was carried out up to 800 °C.

corroborated the compositional homogeneity by giving identical signals from different particles.

BET surface area of the crystalline sample was 20-30 m²/g which is about 50 fold higher than the one for the sample prepared by conventional method. It was observed, in Figure 12, that the BET surface area was dependent on the rate of pyrolysis. The surface area of the crystalline powder was inversely proportional to the heating rate. The elimination of the diffusion barrier was apparently reflected in this unusual behavior. It was suggested that the formation of crystallites at low temperature inhibited the subsequent sintering process. It was reported that the crystallites larger than the size of pores in amorphous mass could trap the pores during the sintering, which raised the porosity of heat treated sample.[37] Upon being heated slowly, the crystallization of the precursor at low temperature should proceed further before the sintering set in. More pores should be trapped if the precursor was heated at lower rate, therby raising the surface area of the crystalline sample. Therefore, by controlling the heating rate, the surface area of the crystalline LSCO may be tailored.

Conclusion

Single phase polycrystalline powder of La₁₋ₓSrₓCoO₃ ($x \leq$ 0.2) was synthesized from polymeric gel precursors made by using PVA as homogenizer. Upon heating the gel, crystallization occurred around 600 °C, which was about 250 °C lower than in conventional solid state reaction. When PVA/metal mole ratio was higher than 3, no minor phase developed during the crystallization: In conventional method, minor phase persisted up to above 1000 °C.

The crystalline product was uniform sized fine particles with average diameter of 100 nm, and had surface area of 20-30 m²/g, which should make it a good candidate for an active catalyst. The surface area could be tailored by adjusting the heating rate.

Decomposition of PVA moieties of the gel completed below 400 °C, thereby eliminating carbonaceous impurities at low temperature. Interestingly, as more PVA was used in preparing the gel, less amount of residual carbon was left in the crystalline product, which is opposite to common expectation. This inversed relationship between initial and final carbon contents suggested that reducing environment was created near the sample during decomposition of the carbonaceous residues.

As larger amount of PVA was used in the gel (conversely, as more carbonaceous residues were left in the precursor), the lattice structure of the La₁₋ₓSrₓCoO₃ heated at 800 °C became more symmetric, being transformed from rhombohedral to cubic. This structural effect disappeared when the cubic sample was further annealed at 1000 °C in air. It was suggested that the local reducing environment generated by the decomposition of the carbonaceous residues above 400 °C induced the oxygen deficiency which resulted in the lattice structure change. The change in the physical properties such as the conductivity and the magnetic susceptibility which may be accompanied by the structural shift would be an interesting facet of this study.

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Selective Transport of Pb(II) Ion by Acyclic Polyethers Bearing Amide End-Groups

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A series of acyclic polyethers bearing amide end-groups and lipophilic alkyl chains (3-5) were successfully synthesized with quantitative yields. Based upon the transport experiment in a bulk liquid membrane (BLM) system and solvent extraction, a very high selectivity of Pb^{2+} over other transition metal cations was observed. Measurement of thermodynamic parameters for complexation in methanol at 25 °C gave a strong evidence for excellent selective complexation for lead ion over other transition metal ions.

Introduction

Acyclic polyethers has been considerably studied due to an excellent complexation behavior although they do not have the pre-organized form to adopt metal ions as do cyclic polyethers.[1-4] So, selective transport of metal cations using acyclic polyethers has long been studied in viewpoints of selective separation, recovery, volume reduction, and selective instrumental sensor applied in most industrial field.[5-7] Especially, selective separation of heavy metal ion such as lead ion from the industrial waste has been remarkably focused.[8,9] We have reported that acyclic polyether 1 in ion selective electrode (ISE) system shows an excellent selectivity of Pb^{2+} over Cu^{2+}.[10] Also, we reported that when dipentyl chains are fixed in nitrogen atom of amide group, increase of lipophilicity e.g. two lipophilic $C_{14}H_{29}$ side chains were attached on α-carbon of carbonyl group (compound 2 in Figure 1) shows decreasing selectivity of Pb^{2+} over Cu^{2+}.[10] However, the thermodynamic parameters such as changes of equilibrium constants, enthalpy changes, and entropy changes of those acyclic polyethers diamide have been not determined so far. Therefore, herein we report the results for the selective transport of Pb^{2+} in bulk liquid membrane and in solvent extraction using organic carrier 3-5 where the hydrogen atom is fixed on the α-carbon

of carbonyl group and the alkyl chain length varies from ethyl to propyl to butyl to study an influence of alkyl chain on amide end-group on metal ion complexation. We also report the results for the determination of thermodynamic parameter for the ligand-metal ion complexation by the use of calorimetric titration method.

Experimental

Chemical Analysis

IR spectra were obtained with a Perkin-Elmer 1600 Series FT-IR on potassium bromide pellet and are recorded in wave number. ^1H NMR spectra were recorded with an AF-300 spectrometer with the chemical shifts (δ) reported down-

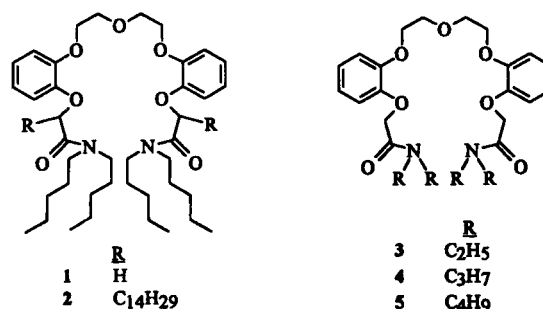**Figure 1.**