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# Mixed-Cation Oxide Powders via Resin Intermediates Derived from a Water-Soluble Polymer

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Submicrometer powders of complex oxides were prepared via resin intermediates based on a starch type of organic precursor. A commercially available water-soluble starch derivative was (for the first time) used as the organic base for solution synthesis of ceramic powders. Calcination of the charred, fluffy, amorphous resins at a temperature below 600°C for 4 h yielded perovskite powders of Sr-doped  $\text{LaMnO}_3$  and Sr-doped  $\text{La}(\text{Fe},\text{Co})\text{O}_3$ . Sr-doped  $\text{LaCrO}_3$  needed to be calcined above 750°C to ensure phase purity and to remove organic residue. Due to the low cost of starch derivatives, the process has the potential of being more economical than the commonly used Pechini's type process, which utilizes citric acid and ethylene glycol.

## I. Introduction

NUMEROUS techniques have been developed for preparing pure, homogeneous, and sinterable mixed-cation oxide powders for electronic ceramics. No one process is universally superior to all others. All powder techniques have their advantages and disadvantages; which is best depends upon what oxide is being synthesized and on its end use. Our method is classified within the general category of solution-synthesis techniques,<sup>1</sup> which start from the formation of a homogeneous aqueous solution followed by particular treatments, e.g., hydrothermal process, coprecipitation, sol-gel route, or formation of a resin intermediate.

Among these solution-synthesis methods, a simple powder process via polymeric precursors consisting of citric acid (CA) and ethylene glycol (EG) was first invented by Pechini.<sup>2</sup> This liquid-mix (LM) process has been extensively used to produce mixed-cation oxide powders with controlled properties for several applications.<sup>3,4</sup> In earlier studies,<sup>5,6</sup> Lessing and Tai varied the organic compositions in this process to prepare perovskite powders whose particle sizes and morphologies were optimized for plasma spraying and tape casting applications, respectively.

Since all organic components involved in a solution synthesis of oxides are eventually burned away, it is desirable to minimize their concentrations and cost. Thus, one of our continued goals about the LM technique has been to replace the current CA-EG polymeric precursors by less expensive organic materials.

Some nonionic polysaccharide-based polymers, for an example: acid hydrolyzed polysaccharide, have been used as industrial gellants for aqueous systems. These starch derivatives have high gelling capabilities and are stable over wide temperature

ranges and pH values. In addition, they are compatible with several ionic salts and, in addition, are capable of forming a polymeric gel, which will foam after reacting with nitric acid or nitrate solution under controlled heating. We have prepared several mixed-cation perovskite powders using selected starch-derived polymers as the main component. Sr(16 mol%)-doped  $\text{LaCrO}_3$  (LSC) powder is of particular interest since this oxide has been used to produce interconnects for solid oxide fuel cells and high-temperature heating elements.<sup>7-9</sup> Sr-doped  $\text{LaMnO}_3$  and Sr-doped  $\text{La}(\text{Co},\text{Fe})\text{O}_3$  are potential cathode materials for solid oxide fuel cells and for solid electrolyte oxygen sensors.<sup>10-12</sup>

## II. Powder Preparation and Characterization

The following example is given using a starch-derived polymer (C3-446 water-soluble polymer, A. E. Staley Co., Decatur, IL) as the only organic constituent of resin intermediate to yield LSC oxide powders. The whole process is illustrated by a flow chart in Fig. 1.

A viscous solution consisting of 20 g of C3-446 polymer and 200 cm<sup>3</sup> of water was first mixed in a beaker. A solution containing all ingredient cations in known ratios for LSC was prepared by dissolving either the nitrates in water, or by dissolving Sr and La carbonates in a weak nitric acid and Cr nitrate solution. The nitrate solution containing 0.1 mol LSC was warmed to 75°C, then added into the beaker of the C3-446 polymeric solution with stirring on a hot plate. This polymer-to-cation ratio, which resulted in the most expanded resin, was determined experimentally in earlier trials. The polymer-nitrate

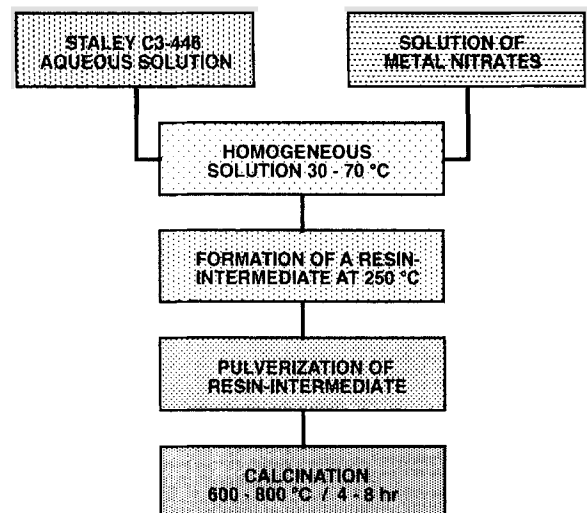
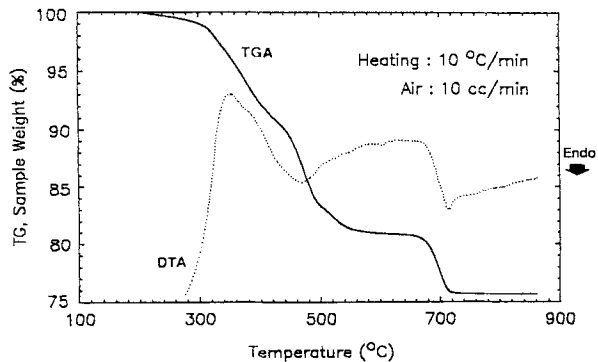


Fig. 1. Flowchart for preparation of mixed-cation oxide powders via resin intermediates.

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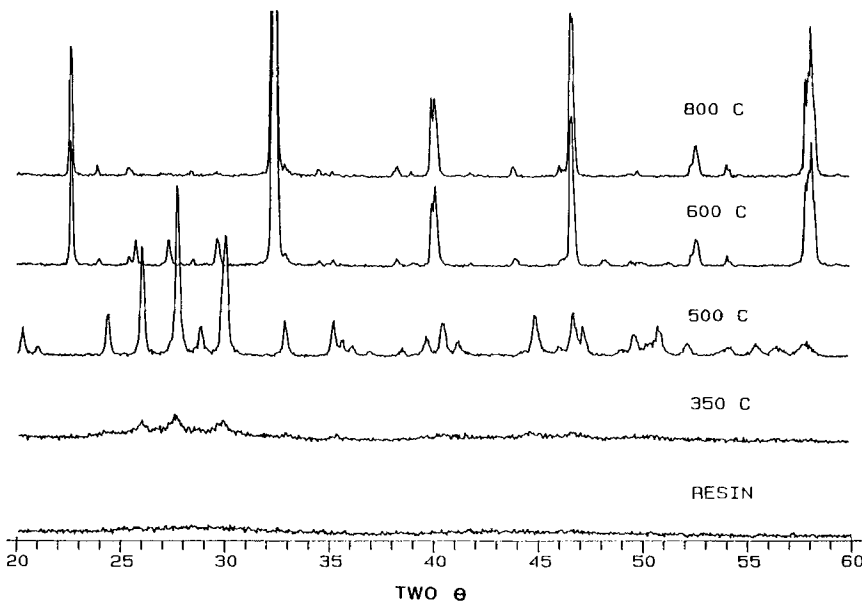
**Fig. 2.** Differential thermal analysis and relative weight loss of resin intermediate for  $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_3$ .

mixture was then gradually heated to 100°C with stirring to evaporate excess water.

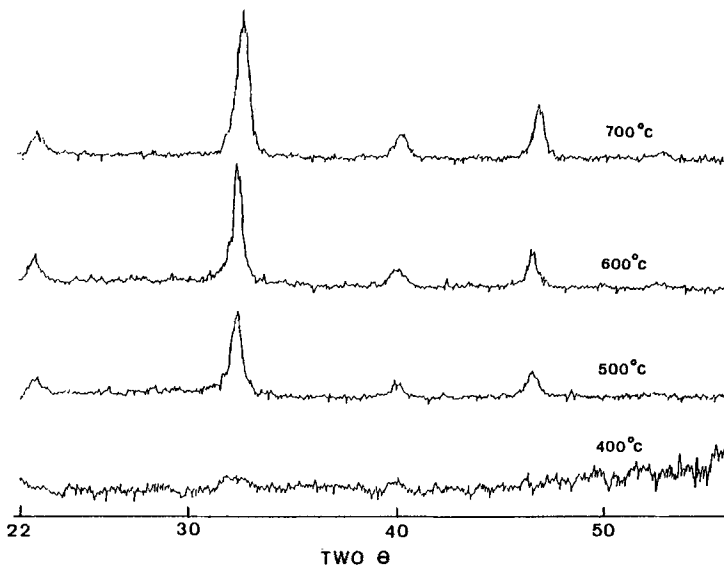
The highly viscous polymer–nitrate solution was then transferred to a porcelain evaporation dish, and the temperature increased to 250°C in a drying oven. As the temperature

increased, the solution started steaming and frothing while the liquid volume decreased. Upon further heating, the gel foamed and released red fumes of nitrogen peroxide. After fuming, a very soft, fluffy, dark resin with large volume was obtained. The apparent volume of this spongelike dry resin was at least 10 times greater than its starting liquid mix. This soft foam was reduced to loose particles by shaking it in a plastic jar.

These resin intermediates of LSC were then calcined to remove organic residues and yield final oxide powders. Calcination was done under flowing air at various temperatures using a previously designed calcination tube.<sup>6</sup> The optimal temperatures for calcining LSC and other oxide powders were determined from thermal analyses and crystallographic characterizations, using a simultaneous thermal analysis system (TG-DTA-DTG STA409, Netzsch Inc., Exton, PA) and an X-ray diffractometer, (XRD-2000, Scintag Inc., Santa Clara, CA) respectively. More detailed crystallographic and microstructural information of the calcined powder was collected by transmission electron (EM300, Philips Inc.) and scanning electron microscopes (JSM-T330A, JEOL Inc.). Chemical purity and cation stoichiometry of final powders were examined using spectroscopic techniques. The amount of residual carbon in the as-calcined powders was estimated from the weight loss of a



**Fig. 3.** X-ray diffraction patterns of resin intermediate for  $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_3$  calcined at the specified temperature for 4 h.



**Fig. 4.** X-ray diffraction patterns of resin intermediate for  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  calcined at the specified temperature for 4 h.

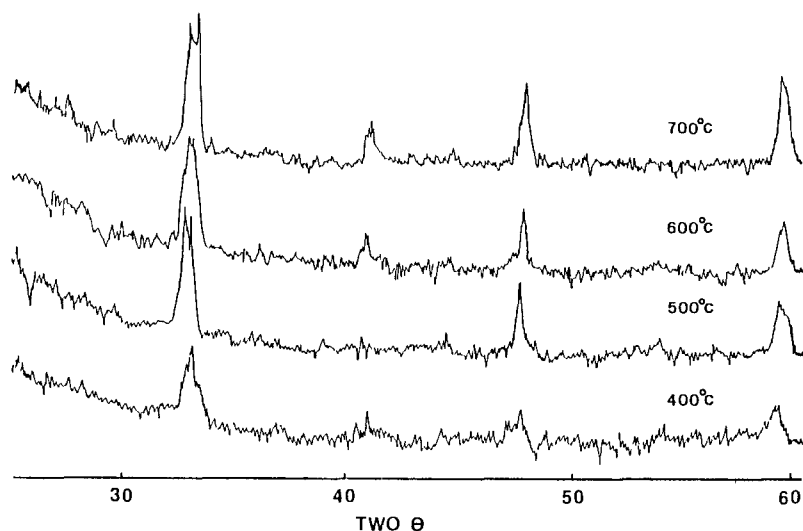


Fig. 5. X-ray diffraction patterns of resin intermediate for  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$  calcined at the specified temperature for 4 h.

sample after annealing at 1000°C for 12 h in oxygen. Particle size distribution and surface area of calcined powders were also analyzed by using standard techniques (CAPA-700 particle size distribution analyzer, Horiba Inc., Irvine, CA; MONOSORB BET surface area analyzer, Quantachrome Co., Syosset, NY). Similar procedures were used in preparing other perovskite-type powders of Sr(15–20 mol%)-doped  $\text{LaMnO}_3$  (LSM) and Sr-doped  $\text{La}(\text{Co}/\text{Fe})\text{O}_3$  (LSCF).

### III. Results and Discussion

The as-charred resin intermediate of LSC was amorphous to X-rays. The TGA/DTA heating curves of a ground LSC resin intermediate (Fig. 2) show a broad exothermic peak, accompanied with a large weight loss, between 300° and 500°C. Such thermal decomposition of organic components before forming crystalline oxides is a typical behavior seen in the LM process.<sup>6</sup> Thus, a slower heating rate, or a longer holding time, during

this stage of calcination should help yield a smooth decomposition of organics without ignition.

The development of LSC crystalline phase as a function of calcining temperature is illustrated by the XRD patterns plotted in Fig. 3. Lanthanum chromate ( $\text{Sr-LaCrO}_4$ ) was formed first starting at 350°C. Lanthanum chromate and lanthanum chromite phases are coexistent until a chromate-to-chromite transition occurs at approximately 700°C. This phase transition caused a weight loss as shown by the TGA curve in Fig. 2. A clean LSC perovskite XRD pattern was obtained by calcining the resin intermediate at 750°C for 4 h. In the case of both LSM and LSCF, no intermediate phases were detected. This is illustrated in Figs. 4 and 5, which show XRD results on resin intermediates for  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$  calcined at the specified temperature for 4 h, respectively. In both cases, well-crystallized perovskite phases formed by 600°C, and these were the only crystalline phases observed.

Although, in most cases, the as-charred resin intermediates were X-ray amorphous, crystallized particles were observed in some resins, using TEM. The selected area electron diffraction pattern and micrograph in Fig. 6 were taken from a resin intermediate for  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$  which had been heated at 250°C for 10 h. The weak ring patterns indicate that crystallites

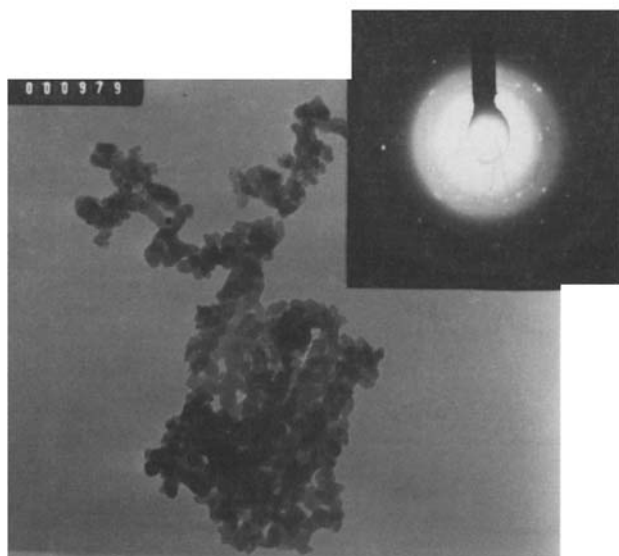


Fig. 6. Transmission electron micrograph and the electron diffraction pattern from the resin of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$  charred at 250°C for 10 h.

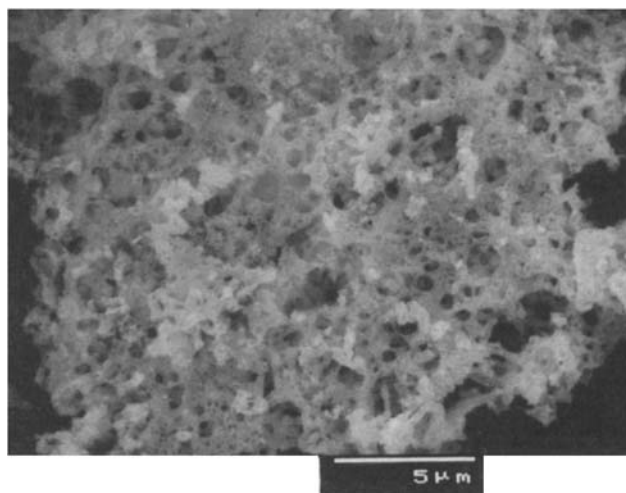


Fig. 7. Scanning electron micrograph of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  powders calcined (at 600°C for 4 h) from the ungrounded resin.

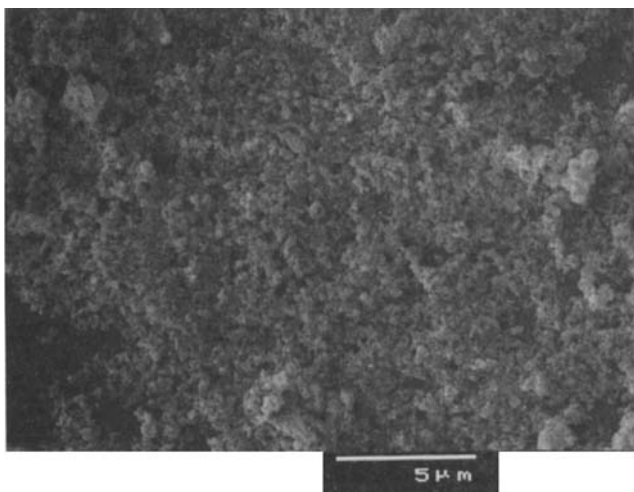


Fig. 8. Scanning electron micrograph of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$  powders calcined at  $700^\circ\text{C}$  for 4 h and ultrasonically dispersed in alcohol.

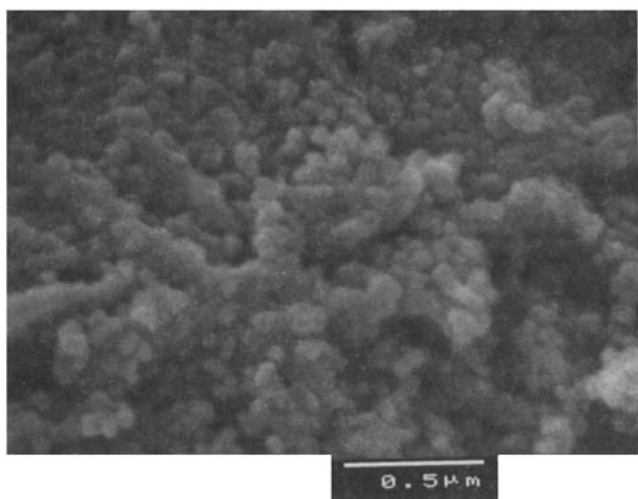


Fig. 9. Scanning electron micrograph (with a higher magnification) of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$  powders calcined at  $700^\circ\text{C}$  for 4 h and ultrasonically dispersed in alcohol.

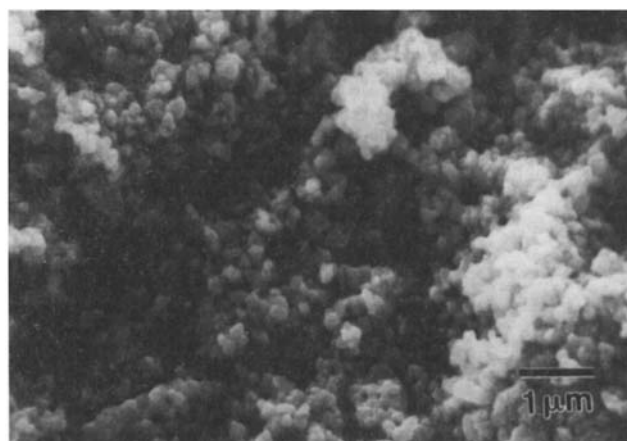


Fig. 10. Scanning electron micrograph of  $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_3$  powders calcined (at  $750^\circ\text{C}$  for 4 h) from a shaken resin.

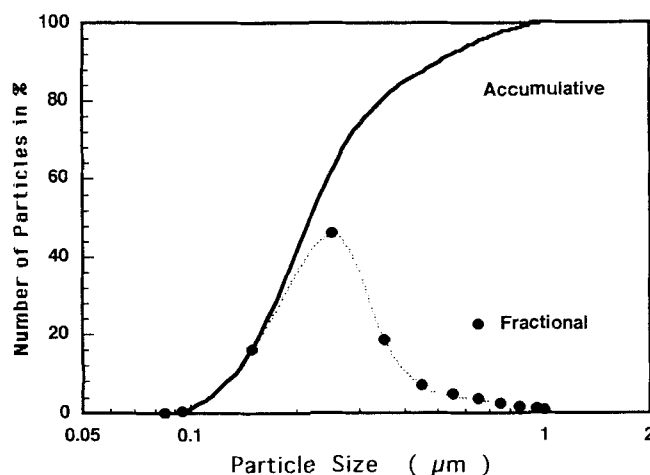


Fig. 11. Particle-size distribution of the as-calcined  $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_3$  powders shown in Fig. 10.

polymer is that it has the potential of lower cost than the process using citric acid and ethylene glycol.

#### IV. Conclusion

A starch-derived polymer has been successfully used to replace citric acid and ethylene glycol in the liquid-mix process.  $(\text{La},\text{Sr})\text{CrO}_3$ ,  $(\text{La},\text{Sr})\text{MnO}_3$ , and  $(\text{La},\text{Sr})(\text{Co},\text{Fe})\text{O}_3$  powders made from this process appear to be equivalent to those derived from the standard liquid-mix process.

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of LSCF, which have a particle size about 0.01 to 0.03  $\mu\text{m}$ , already formed in the charred resin intermediate.

When the oxide powder was obtained from an as-charred resin intermediate without pulverization, it retained the spongelike morphology as seen in Fig. 7. However, these weak agglomerates could be easily broken down to fine particles. SEM micrographs of Figs. 8 and 9 show loose powders of LSCF, which have an average diameter less than 0.1  $\mu\text{m}$ , after ultrasonic dispersion in alcohol. A more appropriate approach was to pulverize LSC resin first, by shaking it with few plastic media in a plastic jar, then to calcine the fine resin intermediate. The resulting oxide powders were fine and loosely interlinked, as seen in the SEM micrograph of Fig. 10. The BET surface area of the LSC powder calcined at  $750^\circ\text{C}$  for 4 h was 8.8  $\text{m}^2/\text{g}$  and the residual carbon was less than 0.2 wt%. The particle-size distribution of this powder was relatively narrow, as shown by Fig. 11.

Results from these studies suggest that a starch-derived polymer (Staley C3-446) can replace citric acid and ethylene glycol in the LM method for oxide powders without losing the superiority associated with this type of process. The chemical reactions occurring in the aqueous mixture of polymer and metal nitrate are being studied, using spectroscopy and other techniques. A very attractive feature of using such a water-soluble

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