SYNTHESIS OF RARE-EARTH-BASED OXIDES FOR THE CERAMIC
INDUSTRY: FROM LABORATORY TO PILOT PLANT*

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SYNTHESIS OF RARE-EARTH-BASED OXIDES FOR THE CERAMIC INDUSTRY: FROM LABORATORY TO PILOT PLANT

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ABSTRACT

A wide variety of compounds, eg., superconductors, chromites, and manganites, have been synthesized by spray drying a mixture of salts or a combination of salts and sols in a flash dryer. The process allows for good control of stoichiometry, morphology, particle size, and surface area. Appropriate particle-growth and synthesis heat treatments of these fine powders were performed. The resultant powders were evaluated for possible applications in fuel cells and superconductors. The processes have been scaled up to a capacity of ≈ 40 Kg a day.

INTRODUCTION

Interest in rare-earth-based oxides for electronic applications has risen dramatically recently. The rare-earth-related oxides are used in high-temperature ceramic superconductors ($\text{YBa}_2\text{Cu}_3\text{O}_x$), interconnection materials (doped LaCrO_3), and cathode materials (doped LaMnO_3) in monolithic solid oxide fuel cells (MSOFC). Most of the research on $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO) superconductors has been performed on samples produced by conventional methods, such as blending stoichiometric amounts of Y_2O_3 , BaCO_3 , and CuO . These solid-state reactions between

constituent oxides and carbonates require long mixing times and high-temperature calcinations with intermittent grindings before homogeneity is obtained. The long and extensive procedures contaminate the final oxide and affect its superconducting properties. A low-temperature process that can reduce the calcination time and the contamination from the grinding media and container would be favorable for realizing high critical current densities and transition temperatures.

Monolithic solid oxide fuel cells are presently under development for a variety of practical applications (e.g., advanced space and aerospace power systems and electric utility power generation). The MSOFC is composed of a honeycomb of very small cells, each 1 to 2 mm in diameter. The walls of the honeycomb are formed from thin (25 to 100 μm) ceramic layers of four cell components [1,2]. The material currently used for MSOFC cathode is Sr-doped LaMnO_3 . The most satisfactory results to date are obtained when two Sr-doped LaMnO_3 powders with differing sinterabilities are used. From the fabrication point of view, it will be advantageous to use one type of powder with desired sinterability. In the MSOFC configuration, adjacent small cells are electrically connected via an interconnection (bipolar) layer. The development of the interconnect for the MSOFC has posed a significant material development challenge because of the particularly demanding set of electrical, mechanical, and chemical requirements for this component. Previous work has identified an acceptor (Mg or Sr)-doped LaCrO_3 as a suitable material, except for the fact that LaCrO_3 , like all Cr-containing oxides, will not sinter to high densities in air. The reason for the low sinterability in these materials is that the predominant mode of mass transport during firing is an evaporation-condensation mechanism which leads to coarsening of the original particles without densification. To obtain high densities, it is necessary to sinter LaCrO_3 to temperatures in excess of 1700°C in a reducing atmosphere [3,4]. However, these conditions are unacceptable for fabrication of the MSOFC for two reasons. One reason is that the interdiffusion of the cell components will become significant at such high temperatures. The other is that the LaMnO_3 will decompose to La_2O_3 and MnO in reducing atmospheres. Given the favorable properties of LaCrO_3 (thermal expansion characteristics, electrical conductivity, and chemical

stability), efforts have been concentrated on developing methods of sintering the material at temperatures below 1400°C in a relatively oxidizing atmosphere. The approach is to synthesize reactive LaCrO_3 powder by a various wet-chemical route [5]. Owing to considerable technological interest in the oxide materials discussed here, it is clear that considerable research must be devoted to the synthesis of these compounds to improve the physical and chemical characteristics of the powders.

EXPERIMENTAL

During its investigation of the synthesis of fine inorganic compounds for the ceramic industry, Rhone-Poluenc reviewed all the processes [6-9] for both chemical and chemical-engineering points of view. Co-precipitation, although attractive for certain applications mostly in the catalysis field, was found to be difficult to control, and extrapolation was a major concern. Furthermore, for each new compound, a study would be needed to control the mixing-nucleation characteristics of the new system. Sol-gel synthesis was found to be too expensive, and classical atomization did not meet the requirements for chemical homogeneity.

To meet the need of the market, Rhone-Poluenc developed a process that is a compromise between classical atomization and the aerosol reactor. The first step in this process is an atomization of a mixture of salts or a combination of salts and sols. A patented spray dryer which operates at higher inlet temperatures (above 700°C) and higher outlet temperature (above 250°C) than classical dryers is used. The system is co-current, with a very short residence times. For the same evaporation capacity, the unit would be smaller than a classical spray dryer. Therefore, the temperature profile in the dryer is very homogeneous. The dryer is an almost perfectly plug-flow reactor, which insures a homogeneous treatment of the particles. The droplet sizes are generated by a two-fluid nozzle, the main advantage of which is that the atomization is made by the hot gases. The dryer design allows for a very fast and homogeneous treatment. As for the classical dryer, the parameters are set to avoid the explosion of the droplets. This process is

simple and can be adapted to many compounds, such as BaTiO₃, YBCO, yttria-stabilized ZrO₂, bismuth-based superconductors, doped chromites and manganites.

The selection of a sol or a salt depends on the compounds (decomposition temperature or melting point of the salts used). It also depends on the morphology and physical properties that are desired in order to obtain a ceramic with an adequate microstructure. Chemical processes allow the control of the size of the colloids, therefore giving a great flexibility to the process. Figure 1 describes the process as applied to the synthesis of YBCO superconductor. A pilot plant unit (capacity up to 8 Ton a year) has been built. Table 1 summarizes the characteristics of the different YBCO grades produced today. As can be seen, the process allows the control of particle size from 0.5 μm up to a few μm . Highly phase pure YBCO (Figure 2) can be produced with a level of impurity phases below the detection level of X-ray diffraction. The calcined product is agglomerated, but a jet milling step is enough to produce sub-micron particles. Any specific composition can be produced; dopants can also be easily incorporated into the composition. A rotary calciner, with a ceramic tube, allows homogeneous calcination. The degree of stoichiometric homogeneity has been found to be around 1 cubic micron when using nitrates. Better homogeneity can be obtained by using different salts. The major advantages of the method, in addition to its flexibility, are the ability to use inorganic compounds in aqueous media and the fact that the raw materials used (nitrates) are not very expensive.

With slight modification of the process, we produced large size batches of Sr-doped LaCrO₃ and Sr-doped LaMnO₃. The surface areas of these powders varied in the range 2-6 m²/g, and processing conditions are optimized to produce powders with any desired size and surface area. These powders are then characterized and evaluated for practical applications.

RESULTS AND DISCUSSIONS

YBCO superconductor powders

The synthesis of YBCO can be achieved by different routes. They can be classified in terms of quality, flexibility, and cost. Almost all of the wet-chemical processes lead to a precursor that must be calcined at temperatures above 850°C to obtain the orthorhombic phase. The powder synthesized by the present method, on the other hand, is phase-pure orthorhombic in the as-synthesized condition [see Fig. 2]. Endothermic or exothermic reactions or melting events associated with impurity phases were identified by differential thermal analysis (DTA) [10]. For the Rhone-Poluenc powder, the only event observed was an onset of melting at $\approx 1020^\circ\text{C}$ due to incongruent melting of YBCO [Fig. 3, curve (a)]. Conventionally processed powder exhibited an endotherm at $\approx 920^\circ\text{C}$, caused by melting of a CuO-BaCuO₂ eutectic [11,12,13], in addition to the endotherm with onset at $\approx 1020^\circ\text{C}$ [Fig. 3, curve (b)]. The phase-pure YBCO powder was uniaxially pressed into long bars ($\approx 9\text{ cm} \times 8\text{ mm} \times 5.5\text{ mm}$) and sintered at $\approx 900^\circ\text{C}$ for 3 h in flowing oxygen at a total pressure of $\approx 7.6\text{ mm Hg}$ (corresponds to a oxygen partial pressure of 10^{-2} atm.). During cooling, the oxygen pressure was increased and samples were annealed at $\approx 450^\circ\text{C}$ for 24 h in flowing oxygen at ambient pressure. The density of sintered samples ranged from 93 to 96% of theoretical value. The transport critical current densities (J_c), measured in zero applied magnetic field at 77 K with a criterion of $1\text{ }\mu\text{V/cm}$ were about 300 A/cm^2 . The measured critical currents in these samples were $\approx 150\text{ A}$. Furthermore, it was found that these samples are relatively less sensitive to moderate applied magnetic field of $\approx 40\text{ G}$. The J_c degraded at a rate of $\approx 0.2\%/G$. For samples made using conventionally processed powders, the value was $\approx 2\%/G$, i.e., the J_c degrades drastically with applied field. Since the microstructures of pressed and sintered pellets are nonuniform and not textured, the limits in J_c that are inherent in the Rhone-Poluenc powders processed in reduced oxygen pressure conditions have yet to be identified.

Sr-doped LaCrO₃

The Sr-doped LaCrO₃, as determined by X-ray diffraction, was found to be phase-pure perovskite structure. The surface area of the powder was $\approx 3.7\text{ m}^2/\text{g}$ and particle size $\approx 0.4\text{ }\mu\text{m}$. The powder was compacted using a pressure of 140 MPa to $\approx 55\%$ of theoretical density. The

compacts were sintered in air at 1400°C for 1 h. The sintered densities were $\approx 90\%$ of theoretical with interconnected porosity. For comparison, pellets made using powders derived by amorphous citrate process, pioneered by Pechini [14], showed sintered densities in the range $\approx 70\%$ of the theoretical value. The interconnect material for use in the MSOFC must have densities $>95\%$ to block the direct inter-mixing of fuel and oxidant gases. Preliminary results indicate that the density of Rhone-Poluenc powder compacts can be increased to $\approx 95\%$ when sintering is carried out at 1550°C, but this temperature is not suitable for MSOFC application—interdiffusion of cell components is a significant problem at these high temperatures. Work is underway to synthesize the powders with increased reactivity to achieve higher densities suitable for MSOFC applications.

CONCLUSION

Considerable research has been devoted to the chemical synthesis of oxide powders to improve the physical and chemical characteristics. We have developed a versatile process applicable to a wide variety of oxides. The YBCO superconductor synthesized by the technique described results in pure orthorhombic powder whereas other wet-chemical techniques yield precursors which need to be calcined at high temperatures. Coprecipitation and classical atomization will have difficulty to maintain a high degree of homogeneity during scale-up. For aerosol processes, the current yields are too low and there is a major concern related to the solid-gas separation system. The Rhone-Poluenc process, by combining the simplicity of the classical atomization with some of the advantages of aerosol processes, is a good cost/quality compromise, which today produces powder in pilot plant quantities. The Sr-doped LaCrO_3 shows considerable improvement over the powder synthesized by the amorphous citrate route. Processing modifications are currently underway in further improving the powder characteristics for use in MSOFC applications.

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FIGURE CAPTIONS

Figure 1. Flow chart describing the process as applied to the synthesis of YBCO superconductor.

Figure 2. X-ray diffraction pattern of phase pure YBCO powder.

Figure 3. Differential thermal analysis traces of YBCO powder (a) synthesized by the Rhone-Poluenec method and (b) conventional solid-state method.

GRADE	PARTICLE SIZE (MICRON)			SURFACE AREA M2.GR	PHASE IMPURITY LEVEL %
	D50	D10	D90		
STANDARD GRADE	1.5	0.5	3	2.5	5-7%
FINE GRADE	0.6	0.25	1.6	2.8	6-8%
PHASE PURE GRADE	1.5	0.75	2.5	2.3	<3%
HIGH DENSITY GRADE	2.3	0.93	4.1	0.4	1%

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