Conf-9105184--4

PNL-SA--19249

DE91 012926

ULTRA-FINE POWDERS USING GLYCINE-NITRATE COMBUSTION SYNTHESIS

L. A. Chick
L. R. Pederson
J. L. Bates
G. D. Maupin

May 1991

Presented at the
Fifth Annual Conference on
Fossil Energy Materials
Oak Ridge, TN
May 14-16, 1991

Work supported by the
U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

DISCLAIMER

ULTRA-FINE POWDERS USING GLYCINE-NITRATE COMBUSTION SYNTHESIS

L. A. Chick, L. R. Pederson, G. D. Maupin and J. L. Bates

Pacific Northwest Laboratory*
Richland, Washington 99352

ABSTRACT

A new combustion synthesis method, the glycine/nitrate process (GNP), is particularly useful for synthesizing ultra-fine, multi-component oxide powders. Examples discussed include La(Sr)CrO_3 and La(Sr)FeO_3 perovskites and a composite of three phases, NiO, $NiFe_2O_4$, and Cu metal.

INTRODUCTION

Fabrication of advanced, multi-functional materials frequently requires the synthesis of complex, ultra-fine powders comprised of a single phase containing several elements (multi-component) or of several phases that are intimately mixed on a micro-scale (composite). Consequently, the success of many promising technologies is entirely dependent upon development of advanced powder synthesis techniques [1]. The challenge presented for these new synthesis techniques is to preserve high powder activity (high surface area) while attaining the desired complex phases. A traditional method for synthesizing a multi-component oxide such as La(Sr)FeO_3, a perovskite of interest for its catalytic properties, is to mechanically mix the requisite oxide or carbonate powders, heat at elevated temperatures until the proper phase is obtained and grind the product. Multiple heating and comminution steps may be necessary to attain the desired level of chemical homogeneity. The correct phase can be obtained in this manner, but high surface area - crucial for catalytic performance - is sacrificed due to particle growth during the prolonged heating [2].

Over the last few decades, a number of oxide ceramic powder synthesis techniques have been developed that begin with preparation of a precursor solution, in which the ions are well-mixed on a molecular scale. These techniques then employ a variety of methods for obtaining solid phases from the precursor solution, the objective being to maintain, as much as possible, the intimate mixing that was present in the precursor. Most often, the first solid product is a physical mixture of crystalline solid intermediate phases that must be thermally reacted to convert to the desired phase(s). The temperature and time required for this final conversion are controlled by the chemistry and crystallite size of the intermediates.

* Operated by Battelle Memorial Institute for the U. S. Department of Energy under contract DE-AC06-76RLO 1830.

Time and temperature, in turn, dictate the crystallite size of the final product. Thus for examples, spray drying, freeze drying, sol-gel and coprecipitation often produce physical mixtures of the individual oxides, hydroxides, carbonates, oxalates, or cyanides, which are then heated to cause decomposition and reaction to the desired multi-component oxide phase [3].

Another group of synthesis techniques seeks to form an amorphous solid intermediate from the liquid precursor. Ideally, the desired crystalline phase is formed directly from the intimately-mixed amorphous solid by local rearrangement of the ions without the need for interdiffusion of species between adjacent solid crystallites. The Pechini [4] or amorphous citrate [5-8] processes form intermediate amorphous solids that are subsequently decomposed and thermally reacted to form complex oxide phases. However, as discussed below, it is often the case that undesirable intermediate crystalline phases form during the extensive thermal treatment required to obtain the final phase.

Recently, several variants of self-sustaining combustion synthesis [9-14] have been developed. Unlike the Pechini or amorphous citrate processes, these self-sustaining combustion processes (including the GNP) are rapid and may closely approach direct conversion from the molecular mixture of the precursor solution to the final oxide product, avoiding formation of intermediate crystalline phases that require interdiffusion for complete reaction. This paper presents a description of the GNP and of several powder products that illustrate the versatility of the GNP method.

PROCESS DESCRIPTION

The GNP consists of two basic steps. First, metal nitrates and a low molecular weight amino acid are dissolved in water. Second, the solution is boiled until it thickens. This viscous liquid ignites and undergoes self-sustaining combustion, producing an ash composed of the oxide product. Most refractory oxides that are composed of a combination of metals having stable nitrates should be possible to synthesize using GNP.

Precursor Solution

The amino acid, glycine, serves two principal purposes: first, it prevents selective precipitation as water is evaporated; and second, it serves as fuel for the combustion reaction, being oxidized by the nitrate ions.

The glycine molecule has a carboxylic acid group at one end and an amine group at the other end, both of which can participate in the complexation of metal ions. Alkali and alkaline earth cations are most effectively complexed by the carboxylic acid group, while many transition metals are most effectively complexed by the amine group. The precursor solutions can typically be boiled down until they reach a honey-like consistency, with no evidence of selective precipitation. Certain precursor compositions,

particularly those containing chromium, become quite acidic (pH<1) when concentrated, so classical complexation of the metal ions may not be maintained. The relatively high solubilities of the metal ions in question as well as the relatively high viscosity of the precursor solution also tend to inhibit inhomogeneous precipitation prior to combustion.

Combustion

Laboratory-scale GNP combustion is done in a fume hood in stainless steel beakers on a hot plate. Approximately 40 ml of the (one molar) precursor solution is burned at a time. Combustion of larger quantities or in confined conditions should be undertaken with extreme caution because of the vigor of the reaction. The hot plate is set on "high", and the solution is simply allowed to boil until it thickens and ignites. Autoignition occurs when the boiling temperature of the precursor solution reaches about 180° to 200°C. The 4 liter beaker is covered with a stainless steel screen to contain the ash.

Unlike the "charring" reaction for the Pechini and amorphous-citrate processes, the combustion reaction for the GNP is rapid, self-sustaining, and essentially complete when the fuel/oxidant ratio is properly adjusted. A typical burn of 40 ml of the precursor solution is completed within a few seconds, although flame temperatures and combustion rates vary widely depending on the product. Figure 1 is a photo of a chromite material being burned in an open dish. The chromite ash can be seen rising in the flame and settling in the surrounding air.

Combustion Redox

For a given product, the main controllable processing variable is the glycine/nitrate (fuel/oxidant) ratio. This ratio affects the flame temperature, the combustion velocity, and the product morphology and composition. Figure 2 shows flame temperature as a function of glycine/nitrate ratio for $La_{.76}Sr_{.24}CrO_3$. Flame temperatures were measured by a two-color optical pyrometer focused on the glowing ash during combustion in an open petri dish, such as that shown in Figure 1. The peak flame temperature, about 1450°C, is obtained at a glycine/nitrate (molar) ratio of 0.552. This ratio corresponds to combustion reactions that produce H_2O, CO_2, and N_2 with no atmospheric oxygen required and is hereafter referred to as the stoichiometric ratio. For a product in which the metal cation(s) has the same valence in the nitrate precursor as in the oxide produced, the stoichiometric glycine/nitrate molar ratio is 5/9. However, the optimum powder product is not always obtained at the stoichiometric glycine/nitrate ratio. In the following discussions of GNP powders, the effects of altering the glycine/nitrate ratio are examined.

Figure 1. Photo of a typical glycine / nitrate combustion for La(Sr)CrO_3. Ash particles are seen rising through the combustion plume.

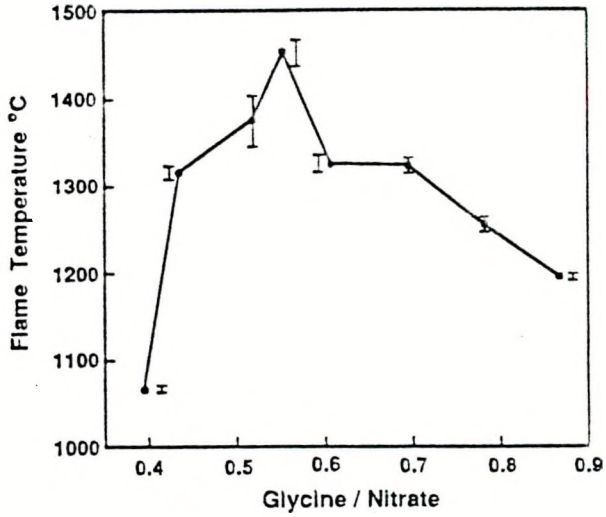


Figure 2. Flame temperatures measured by two-color optical pyrometry for the combustion of glycine / nitrate La(Sr)CrO_3 precursors prepared at various glycine / nitrate ratios.

POWDER CHARACTERISTICS

La(Sr)CrO_3 Perovskite

Lanthanum strontium chromites, La(Sr)CrO_3 (LSC), having the generalized (ABO_3) perovskite structure, are of considerable technological interest because of their electrical conductivity and chemical/thermal stability. The chromites have been investigated for use in high-temperature furnace electrodes, solid oxide fuel cells, and magnetohydrodynamic reactors. Recently, the most common technique for synthesizing these compounds has been the liquid-mix (amorphous citrate) process [5].

Figure 3 shows x-ray diffraction (XRD) patterns for LSC ash produced at three glycine/nitrate ratios. The sample labeled fuel-lean contained one half the glycine required for the stoichiometric ratio, while the sample labeled fuel-rich contained double the stoichiometric glycine level. Reference to Figure 2 shows that the flame temperatures of the fuel-rich and fuel-lean samples (not specifically measured for the subject samples) must have been several hundred degrees below the 1450° C stoichiometric flame temperature. The sample prepared at the stoichiometric ratio is fully crystalline perovskite with average crystallite size near 20 nm, as determined by XRD line-broadening. The fuel-lean sample is largely amorphous with a trace of crystalline strontium nitrate. The fuel-rich sample is mostly amorphous, containing some perovskite crystals with an average size significantly less than 10 nm.

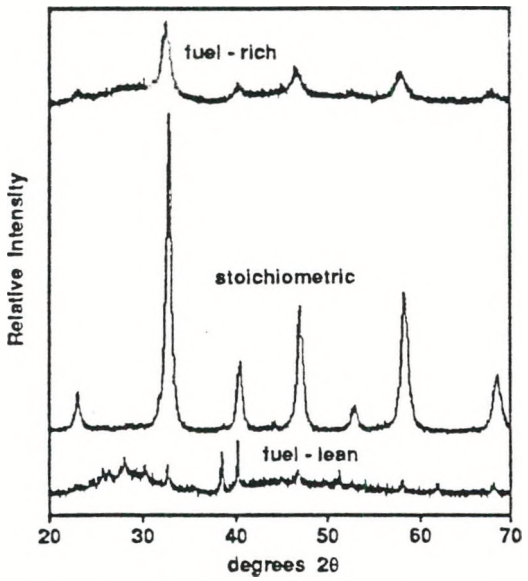


Figure 3. XRD patterns for LSC ash combusted under three glycine / nitrate ratios. Stoichiometric burn produced crystalline perovskite only. Fuel-rich produced the perovskite (smaller crystals) and amorphous material. Fuel-lean produced mainly amorphous material with a minor amount of strontium nitrate.

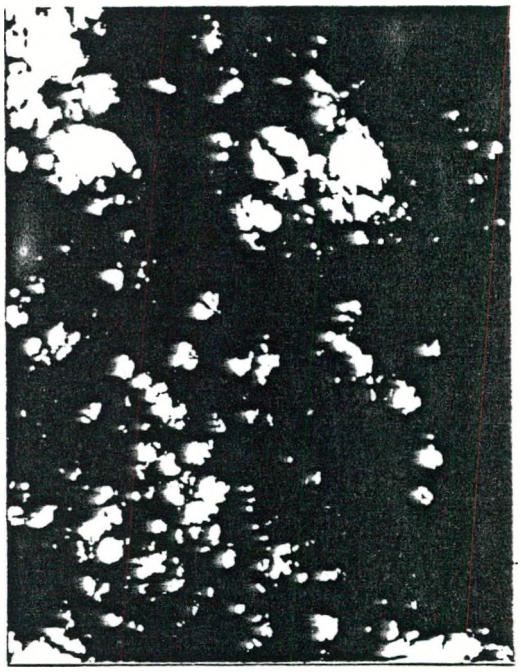


Figure 4. Brighfield TEM of fuel-lean LSC ash.

Figures 4-6: 40 nm

Figure 5. Brighfield TEM of stoichiometric LSC ash.

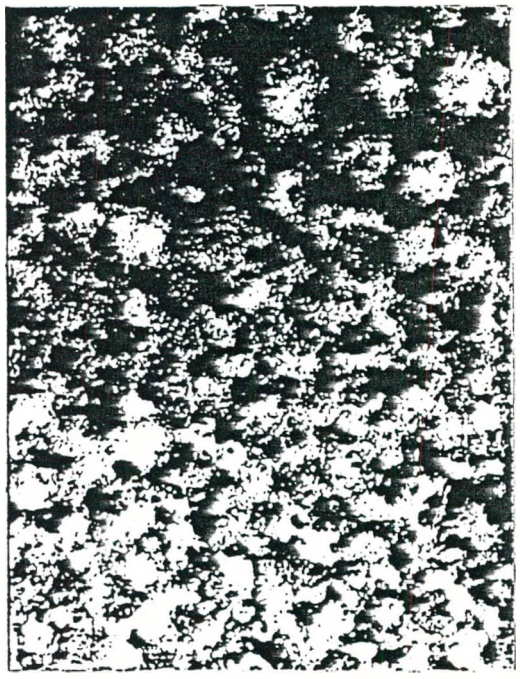


Figure 6. Brighfield TEM of fuel-rich LSC ash.

Figures 4 through 6 are brightfield transmission electron micrographs (TEM) of the LSC samples. These images correlate well with the XRD data in Figure 3. The fuel-lean sample, Figure 4, is composed of amorphous bubbles. The stoichiometric sample, Figure 5, is composed entirely of crystalline particles, all near 20 nm. The fuel-rich sample, Figure 6, apparently represents a stage of crystallization between the lean and the stoichiometric; that is, small crystallites (well under 10 nm) have begun to form in the bubble walls, but much amorphous material remains.

Energy dispersive microanalysis (EDS) was performed on 20 individual LSC crystallites (stoichiometric combustion) using a TEM. The results [9] establish that the chemical composition of the GNP-produced LSC powder does not vary by more than +/- 5% from crystallite to crystallite. In contrast, LSC produced by the amorphous-citrate process [6] shows extensive compositional variability, even after one hour of calcination at 1060°C. Several intermediate solid phases were detected in the amorphous-citrate material prior to and during the calcination [6]. The extensive thermal treatment required to chemically homogenize the amorphous-citrate product results in crystallite growth, reducing the activity of the powder.

$La(Sr)FeO_3$ Perovskite

Lanthanum strontium iron cobalt perovskites, $La(Sr)Fe(Co)O_3$, have been investigated as catalysts for the combustion of methane and n-butane [15]. Specific surface areas of these perovskites are in the range of 3 to 7 m^2/g when they are produced by calcination of an aqueous solution of lanthanum and strontium acetates and iron nitrate [15]. The composition, $La_{0.8}Sr_{0.2}FeO_3$, (LSF) was produced by GNP using a range of glycine/nitrate ratios. General results are similar to those for $La(Sr)CrO_3$ (above), except that crystallite sizes are larger and the fuel-rich sample appears to be fully crystalline. Figure 7 shows XRD for three redox conditions. Line broadening measurements yield an average crystallite size of 20 nm for the fuel-rich material and 30 nm for the stoichiometric sample. The fuel-lean sample appears to be largely amorphous, with a minor amount of strontium nitrate. TEM microstructures are consistent with the XRD data.

Specific surface areas for five of these samples, measured by multi-point BET, range between 6 and 28 m^2/g. These BET results, Figure 8, are generally consistent with the XRD and TEM. The smallest surface area is obtained for the stoichiometric condition, which yields the largest crystallite. Samples produced under off-stoichiometric conditions, either fuel-lean or fuel-rich are either (respectively) amorphous or have smaller crystallite sizes, so can be expected to have larger surface areas.

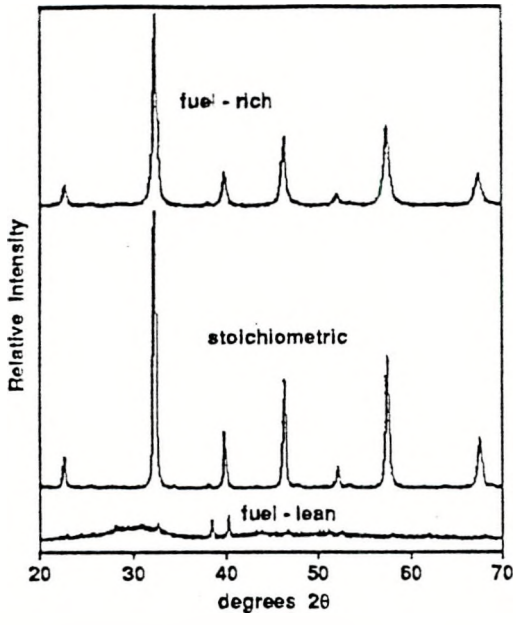


Figure 7. XRD patterns for LSF ash combusted under three glycine / nitrate ratios. Fuel-rich and stoichiometric burns produced crystalline perovskite only, the former having smaller crystallite size. Fuel-lean produced mainly amorphous material with a minor amount of strontium nitrate.

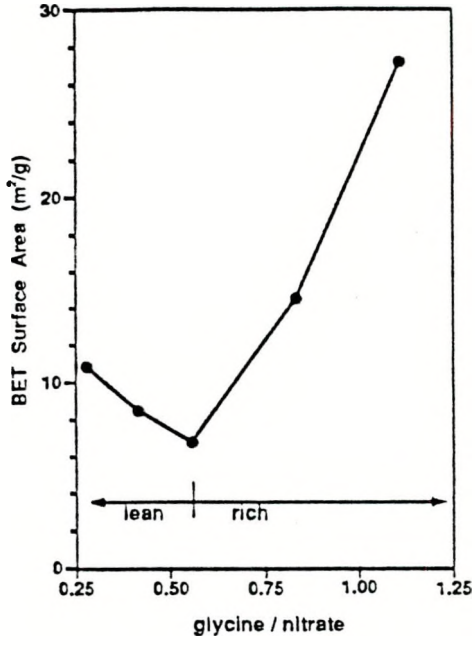


Figure 8. Specific surface areas for the LSF ash products, determined by multi-point BET.

$NiO\text{-}NiFe_2O_4\text{-}Cu$ Composite

A ceramic/metal composite (cermet) composed of two ceramic phases, NiO and $NiFe_2O_4$ (spinel) and copper metal is under investigation as an alternative to the consumable carbon anodes in the production of aluminum. In the past, this composite has been produced by mechanically mixing powders of the three phases, pressing and sintering at 1250° C. Recently, GNP was employed with the objective of decreasing the scale of the composite microstructure.

For the production of this composite, the fuel-rich and the stoichiometric conditions both produced powders containing Ni-Fe metal alloy, NiO, CuO, and $NiFe_2O_4$, as determined by XRD. The fuel-lean combustion produced CuO, NiO and $NiFe_2O_4$. The XRD line-broadening measurements and TEM indicate that the fully oxidized powders (fuel-lean) had significantly smaller crystallite size than those containing the metal phase. Use of the fully oxidized powder to fabricate the cermet necessitated a heat treatment to reduce the CuO, but this could be conducted at a low enough temperature to prevent melting and excessive crystallite growth, thus maintaining the desired fine crystallite size.

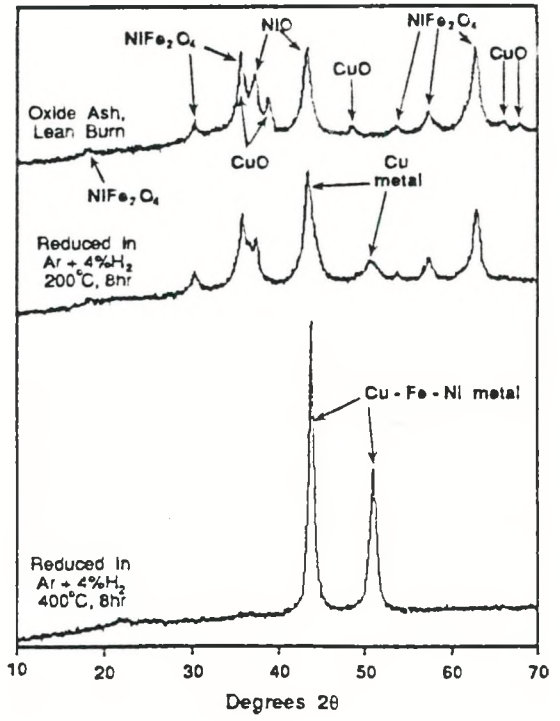
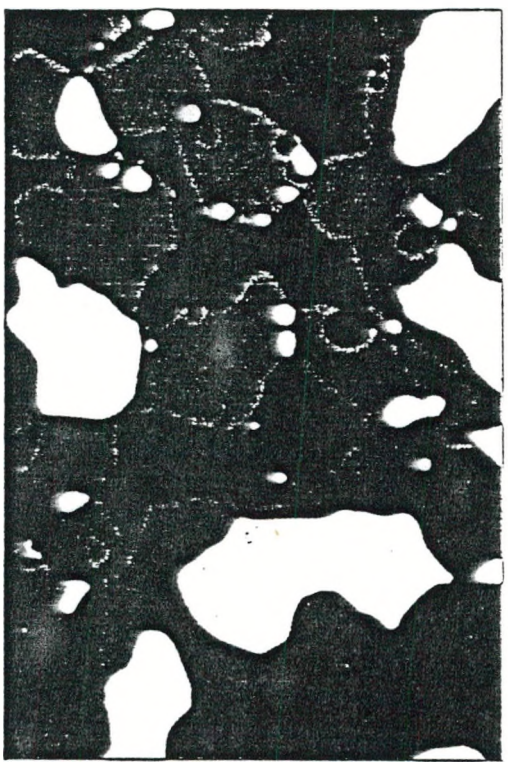


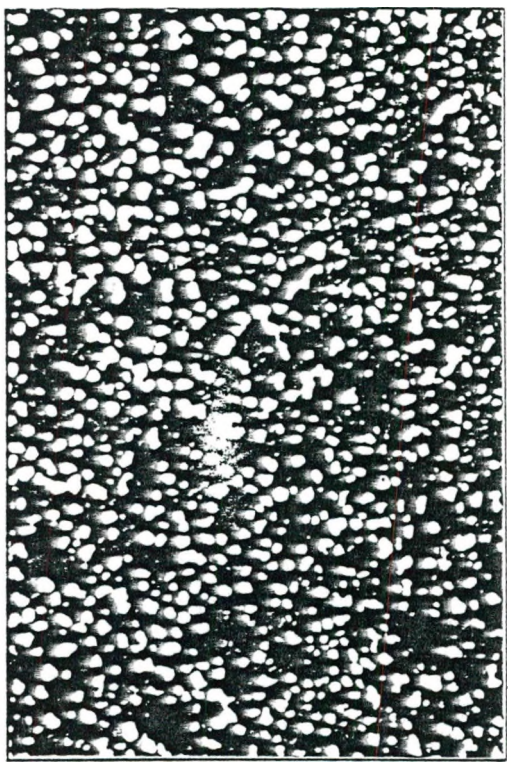
Figure 9 (left). XRD patterns: top pattern is for fuel-lean ash product, composed of CuO, NiO, and $NiFe_2O_4$; middle pattern is for 200°C reduced powder, composed of Cu metal, NiO, and $NiFe_2O_4$; bottom pattern is for 400°C reduced powder, composed of a single Cu-Ni-Fe metal alloy.

Figure 10 (bottom left). Optical micrograph of sintered composite made by the standard method of mechanically mixing powders, sintered at 1250°C, 8 hours.

Figure 11 (bottom right). Optical micrograph of sintered composite made by GNP, sintered at 1130°C, 1 hour. Overall composition is the same as the material in Figure 10.

Figures 10, 11: 10 μm





After combustion to produce the ash under fuel-lean conditions, the powder was heated in an atmosphere containing 4% H_2 in Ar. Figure 9 shows XRD patterns for the oxide ash before (top) and after two different reducing heat treatments. Eight hours at 200°C in Ar + 4%H_2 reduced the CuO to Cu metal, but left the NiO and $NiFe_2O_4$ intact, whereas a similar treatment at 400°C reduced all of the oxides to a single cubic metal phase. Intermediate temperature reductions result in the partial incorporation of Ni into the Cu metal phase. After completion of the desired reducing heat treatment the powder was isostatically pressed at 20,000 psi and sintered at 1130°C for one hour in dry nitrogen.

Figures 10 and 11 compare the microstructures of a typical anode made by the standard powder method to that of the same composition made using GNP. On a linear basis, the scale of the GNP-produced microstructure is about an order of magnitude smaller than that produced by the standard method. On a volume basis, the GNP particles within the composite are about three orders of magnitude smaller.

CONCLUSIONS

The glycine-nitrate process is a promising method for the production of a wide variety of compounds that contain elements having stable nitrates. The GNP is particularly appropriate for synthesis of multi-component, single phase materials and for multi-phase composite materials.

REFERENCES

1. National Research Council, Materials Science and Engineering for the 1990's: Maintaining Competitiveness in the Age of Materials. National Academy Press, Washington, D. C. (1989).

2. R. J. H. Voorhoeve, D. W. Johnson, Jr., J. P. Remeika, and P. K. Gallagher, Science, 195 (1977) 827.

3. L.G. Tejuca and J. G. Fierro, Advances in Catalysis, 36 (1989) 237.

4. M. P. Pechini, US Patent 3,330,697 (1967).

5. N. G. Eror and H. U. Anderson, in: Better Ceramics Through Chemistry, II. Mat. Res. Soc. Symp. Proc., Vol 73. Edited by C. J. Brinker, D. E. Clark, and D. R. Ulrich. Mat. Res. Soc., Pittsburgh, PA (1986) pp. 571-77.

6. D. J. Anderton and F. R. Sale, Powder Metallurgy, 22 (1979) 8.

7. M. S. Baythoun and F. R. Sale, J. Mater. Sci. 17 (1982) 2757.

8. P. A. Lessing, Ceramic Bulletin 68 (1989) 1002.

9. L. A. Chick, L. R. Pederson, G. D. Maupin, J. L. Bates, L. E. Thomas and G. J. Exarhos, Mater. Lett. 10 (1990) 6.

10. P. Ravindranathan and K. C. Patil, J. Mater. Sci. Lett. 5 (1986) 221.

11. P. Ravindranathan and K. C. Patil, Am. Ceram. Soc. Bull. 66 (1987) 668.

12. P. Ravindranathan G. V. Mahesh and K. C. Patil, J. Solid State Chem. 66 (1987) 20.

13. J. J. Kingsley and K. C. Patil, Mater. Lett. 6 (1988) 427.

14. J. J. Kingsley, S. Sudar Manoharan, K. Suresh and K. C. Patil, in: Proceedings of the 2nd International Conference on Ceramic Powder Processing Science, eds. H. Harsner, G. L. Messing and S. Hirano (Deutsche Keramische Gesellschaft, 1988) p. 343.

15. H. M. Zhang, Y. Shimizu, Y. Teraoka, N. Miura and N. Yamazoe. J. Catalysis, 121, pp. 432-40 (1990).