

PREPARATION AND CHARACTERIZATION OF CERAMIC FINE POWDERS PRODUCED BY THE EMULSION PROCESS

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ABSTRACT

A variety of uniform fine ceramic powders were prepared from an aqueous phase, dispersed in an oil emulsion matrix. Simple to complex compounds could easily be produced with nearly monosphere morphology, ranging between 200nm and 1000nm. The size and distribution of the emulsified spheres can be adjusted to a certain degree by the concentration of the salt in the aqueous solutions and by emulsification pressure. This process is quite versatile and ideal for preparing complex chemical compounds where stoichiometry and small dopant additives can have a significant effect on the sintering characteristics and corresponding physical and electrical properties.

Among the materials that have been prepared and characterized are the following:

- Titanates - (BaTiO_3 , SrTiO_3 , BaTi_4O_9 , $\text{Ba}_2\text{Ti}_9\text{O}_{20}$)
- Doped Titanate - (Mn, La, BaTiO_3)
- Oxides - (Al_2O_3 , Nb_2O_5 , Bi_2O_3 , Mn_2O_3)
- High Temperature Superconductors - $\text{YBa}_2\text{Cu}_3\text{O}_7$

The properties of some of these materials will be reported in the near future.

1. INTRODUCTION

The driving forces for this research were the need to produce simple and complex ceramic fine powders with high chemical purity, uniform particle size in the range of 0.1 to 1.0 micron, and the ability to manipulate the composition to meet certain physical and electrical properties. The commercial applications of these powders were mainly focused on multilayer ceramic capacitor technology. These efforts were initiated by the R&D group of the Sprague Electric Company in the early 1980's.

There are several research and commercial processes for producing fine ceramic powder via the chemical route. Recently Hilton and Frost [1] published a comprehensive survey of the various chemical processes for

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producing barium titanate. Depending on the particular application, there are advantages and disadvantages to each process. Similarly, Page et al [2] have characterized the sintering behavior of fine powder barium titanate prepared by various syntheses. These processes include citrates, oxalate, sol-gel, hydrothermal and other exotic methods.

Kanai et al [3] reported on the preparation technique of $2\text{ZrO}_2 \cdot \text{Yb}_2\text{O}_3$ by the emulsion process, while Richardson and Akinc [4] described the preparation of spherical yttrium oxide powders using emulsion evaporation.

Accordingly, the objective of this paper is to report on the preparation and characterization of various ceramic powders made by the emulsion process with emphasis on barium titanates.

2. EXPERIMENTAL PROCEDURES

A series of three issued patents [5-7] describes a procedure, based on the use of emulsion technology, for the preparation of ceramic powders having controlled particle size distributions. The process is general for many ceramic powders or combinations of ceramic powders for which water soluble precursors are available. The aqueous solution of ceramic precursors is emulsified with an organic fluid containing an organic surfactant to provide a dispersion of aqueous droplets of nearly uniform size in the organic fluid. Since the original aqueous solution is homogeneous and the dispersed water droplets in the organic phase are uniform in size, each water droplet will contain essentially the same amount of ceramic materials. The aqueous phase and oil phase are pre-mixed in the proper ratios using a high shear mixer. A dual head metering pump feeding a Hydroshear module may be used for large volumes. To complete the emulsion the premixed solution is processed through a two-stage homogenizer capable of operating at 5000 psi ($\approx 34\text{MPa}$). The uniformity in size of the resultant $0.1\mu\text{m}$ to $0.3\mu\text{m}$ particles is largely dependent upon proper mixing and homogenizer operating parameters.

The emulsion is reduced in volume using typical vacuum distillation methods to remove the water and most of the organic fluid. This may be accomplished either by using a laboratory set-up for small quantities or using a continuous feed thin film evaporator for larger needs. This yields a slurry of ceramic precursor particles held together by the surfactant and the small amount of still resident organic fluid.

The resultant slurry is pyrolyzed in a retort furnace with a reduced air atmosphere to convert the slurry into an amorphous char. This maintains the separation between the dried spherical particles and prevents the formation of sintered or fused agglomerates. Photomicrographs in Fig. 1a & 1b show the uniformity and spherical shape of the pyrolyzed material.

The char is calcined under controlled conditions to burn off the carbon while minimizing the formation of agglomerates. This may be done easily using a belt or rotary tube furnace. The calcined product may be milled or jet pulverized to separate agglomerates that may be formed during calcining.

A typical flow chart for the preparation and process for barium titanate is shown in flow chart 1.

3. CHARACTERIZATION

3.1 BaTiO_3 and Doped BaTiO_3

As a ceramic capacitor manufacturer, Sprague Electric's major goal was to evaluate various preparations of high purity fine powder barium titanate. As noted earlier, the emulsion process was chosen because of its versatility and can be scaled up to large production quantities.

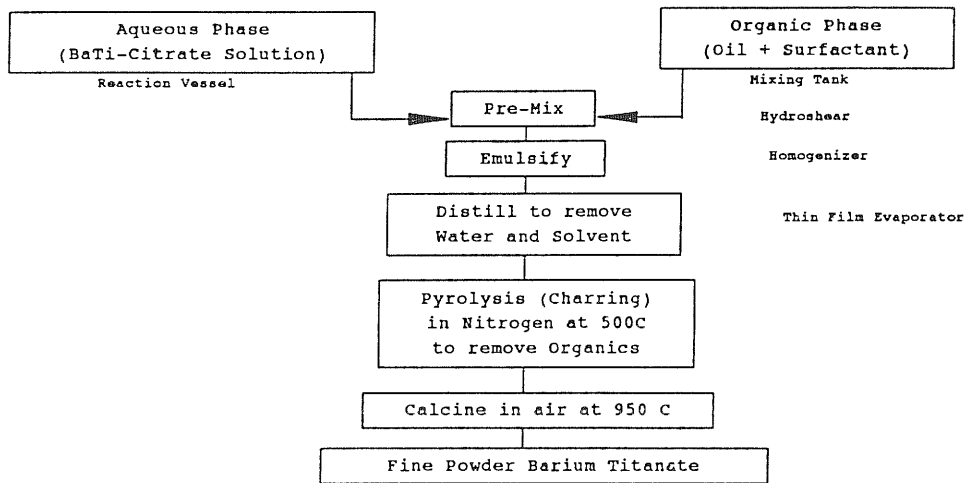
For the capacitor technology, the ability to adjust the stoichiometry (Ba/Ti ratio) and to introduce certain dopants and/or modify the composition on an atomic level, have significant effect on the sintering behavior and electrical properties of various classes of dielectrics. For example, a barium titanate base dielectric for high permittivity Y5V or Z5U application will require uniform solid solution between the BaTiO_3 , the T_c shifter, such as SrZrO_3 , and the dopants, such as Mn_2O_3 .

On the other hand, composition for X7R application requires a limited solid solution on the surface of the grain between BaTiO₃ and the additives. In this case, the sintered specimen is usually fine grained with core/shell structure.

The emulsion process was found to be ideal for adjusting the Ba/Ti in the range of 0.97 to 1.03 and introducing dopants into the precursors salt solution, such as Mn, La, Nb, and Boron, and many other elements. A flow diagram for producing BaTiO₃ from an aqueous phase of barium-titanium-citrate solution is shown above. Fig. 1a shows the morphology of the char powder (after pyrolysis in N₂ at 500°C) and Fig. 1b shows the morphology after calcining in air at 750°C. Fig. 1c shows the corresponding x-ray diffraction patterns of both powders. In the char state, the powder is amorphous. Thermogravimetric analysis of a stoichiometric composition, after the char stage, is shown in Fig. 2. The transition from amorphous to crystalline state between 550 and 690C corresponds to about 1.1w% loss of carbon residue.

It is important to note that the nearly spherical grains tend to retain their morphology, even at 1100°C calcine temperature. The surface area of a stoichiometry BaTiO₃ decreases with calcine temperature from 11.5M²/g at 700°C, to 7.25 at 950°C, to 3.5 at 1100°C.

The effect of stoichiometry (Ba/Ti) on the physical properties of the powder and corresponding electrical properties of sintered specimen are described in Table 1. A slight deviation in stoichiometry has a significant effect on the microstructure and grain growth. A stoichiometric composition could be sintered to a high



Flow Chart 1. Preparation of Barium Titanate by Emulsion method

Design Ba/Ti ratio	1.00	1.015	0.985
Calcination Temperature °C	950	950	950
Powder Surface Area (Sq.M/gm)	7.0	4.1	5.2
Sintering Temperature °C	1300	1300	1300
Microstructure	Uniform Grains 2 to 4 microns	Exaggerated Grain Growth 20 to 30 micron grains in Fine Grain Matrix	Large Grains 30 to 50 microns Ti rich minor phase
Dielectric Constant at 1KHz, 1Vrms, 25°C	3000	2500	1700
Curie Point °C	127±2	127±2	127±2

Table 1. Effect of Stoichiometry (Ba/Ti ratio) on properties of disk samples.

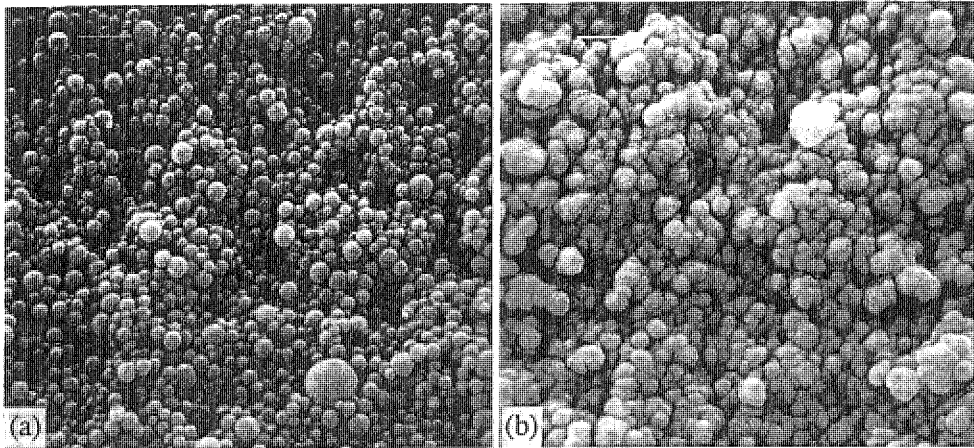


Figure 1a & 1b. Microstructure of BaTiO₃ prepared by emulsion method.

(a) Char 10000x Bar=1μ
 (b) After calcination at 750°C. 10000x Bar=1μ

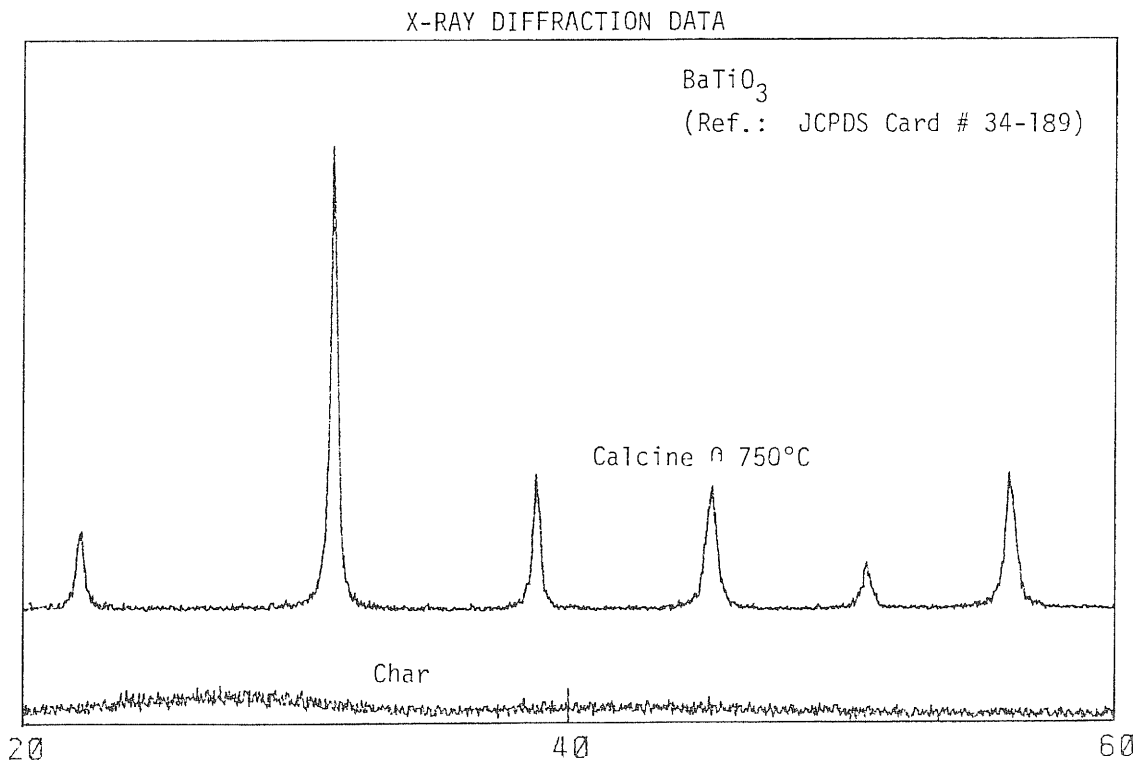


Figure 1c. X-ray diffraction pattern of BaTiO₃ char, and powder calcined at 750°C.

density, as low as 1250°C, with uniform grains ranging between 2 and 3μm. The composition with excess Ba showed exaggerated large grain (10-20μm) in fine grain matrix (1-2 μm). The composition with excess titanium showed very large grains (30-50 μm) and clear evidence of second phase rich in TiO₂. These results are consistent to those reported by other processes.

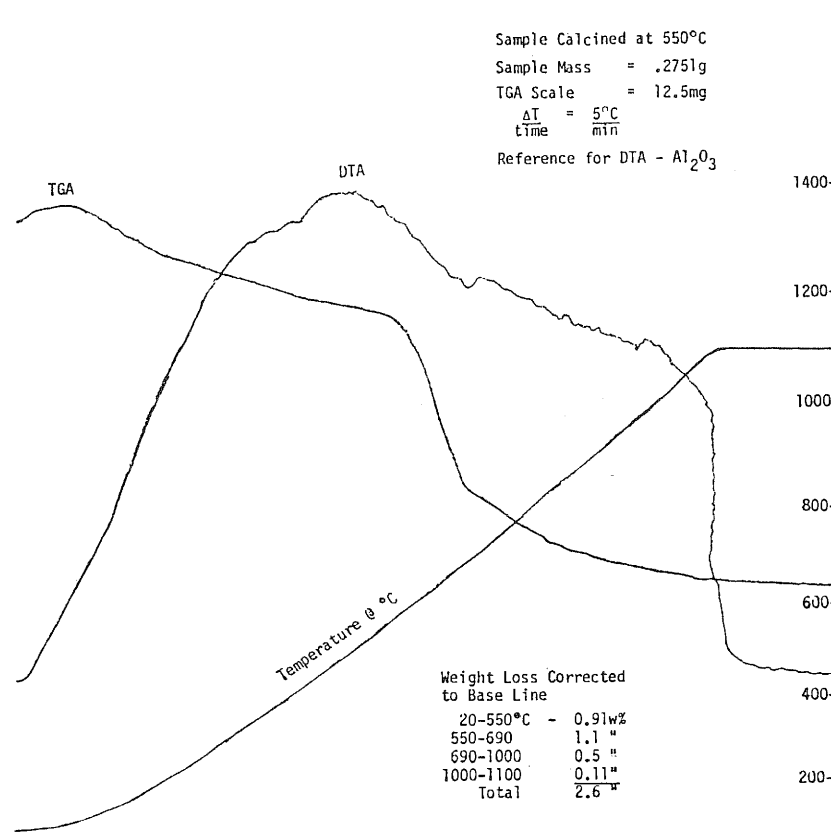


Figure 2. TGA and DTA traces of BaTiO_3 powder after char stage.

3.2 BaTi_4O_9 and $\text{Ba}_2\text{Ti}_4\text{O}_{20}$

The high titanate phases in the BaO-TiO_2 system have been found to possess excellent electrical properties for microwave application [8]. Achieving the exact compositions of these higher titanates by the standard mixing and calcination of $\text{BaCO}_3 + \text{TiO}_2$ has been reported to be quite difficult.

Fukui et al [9] prepared $\text{BaTi}_5\text{O}_{11}$ ceramics from alkoxide-derived powder. They showed that this compound will decompose to $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ and rutile TiO_2 when the sintering was done at a heating rate of $100^\circ\text{C}/\text{min}$.

BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ were prepared by the emulsion process in a similar fashion to that of BaTiO_3 described above. Fig. 3a shows the powder morphology after 1050°C calcining while Fig. 3b shows the x-ray diffraction of single phase BaTi_4O_9 , calcined to 1050°C . Similarly, the powder morphology and x-ray diffraction of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ are shown in Figs. 4a and 4b, respectively.

3.3 Nb_2O_5

Niobium pentoxide is a common additive in many capacitor dielectric compositions. In small quantity ($<0.1\text{a}\%$) doping of Nb in BaTiO_3 will render it semi-conducting. Such a system has been used for PTCR application. Addition of larger quantity (0.5 to 1.5a%) to BaTiO_3 powder can have significant influence on the grain growth and ultimate electrical properties of the dielectric. Such a system is commonly used for X7R ceramic capacitors. To achieve optimum properties with minimum Nb_2O_5 addition, it is highly desirable that the particle size be uniform and small, $<0.5 \mu\text{m}$. The emulsion process has been found to be ideal for producing uniform powder. Fig. 5a shows the morphology of the powder after 950°C calcine. While Fig. 5b shows the x-ray diffraction pattern of the char (after 450°C in N_2) and after 750°C calcining in air. The transition from amorphous to crystalline structure occurs between 575 and 650°C . The structure is that of a low temperature phase of Nb_2O_5 .

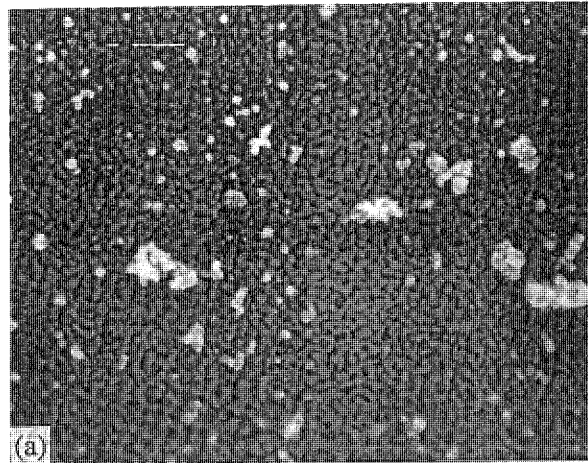


Figure 3a. Microstructure of $BaTi_4O_9$, prepared by emulsion method.
10000x Bar = 1μ

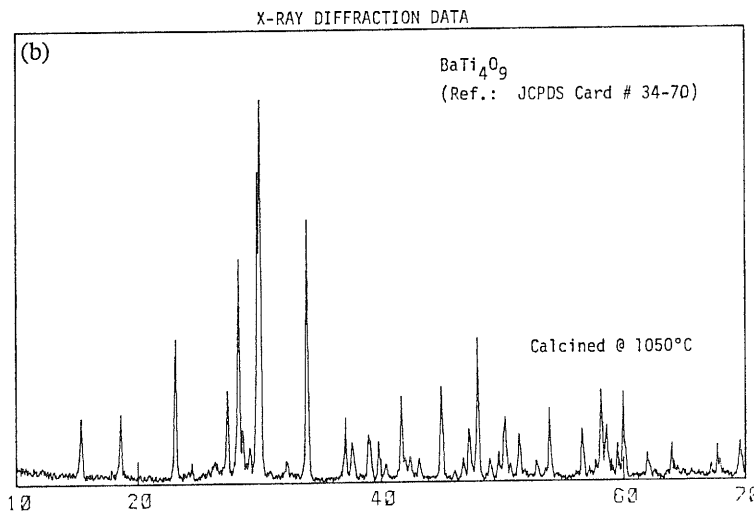


Figure 3b. X-ray diffraction pattern of $BaTi_4O_9$ powder calcined at $1050^\circ C$.

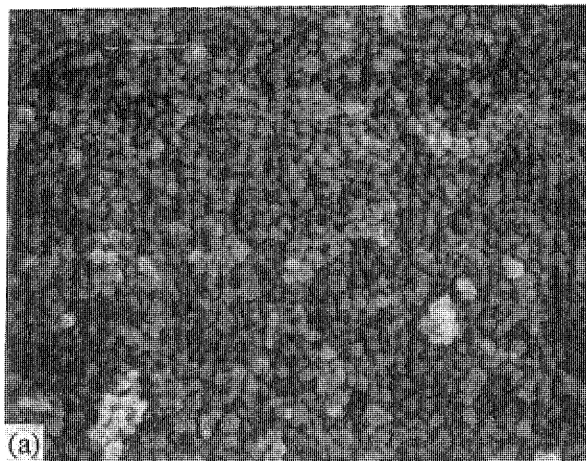


Figure 4a. Microstructure of $Ba_2Ti_9O_{20}$ prepared by emulsion method.
10000x Bar = 1μ

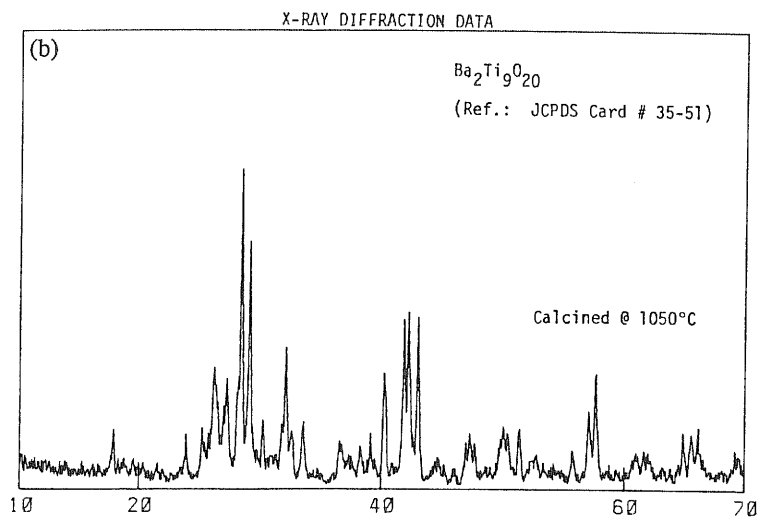


Figure 4b. X-ray diffraction pattern of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ powder calcined at 1050°C.

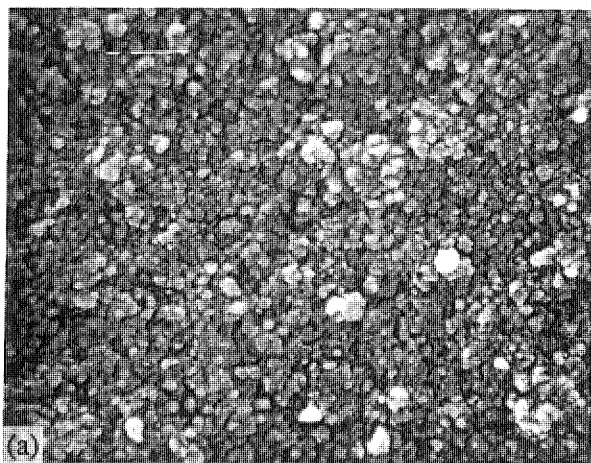


Figure 5a. Microstructure of Nb_2O_5 prepared by emulsion method.
10000x Bar = 1 μ

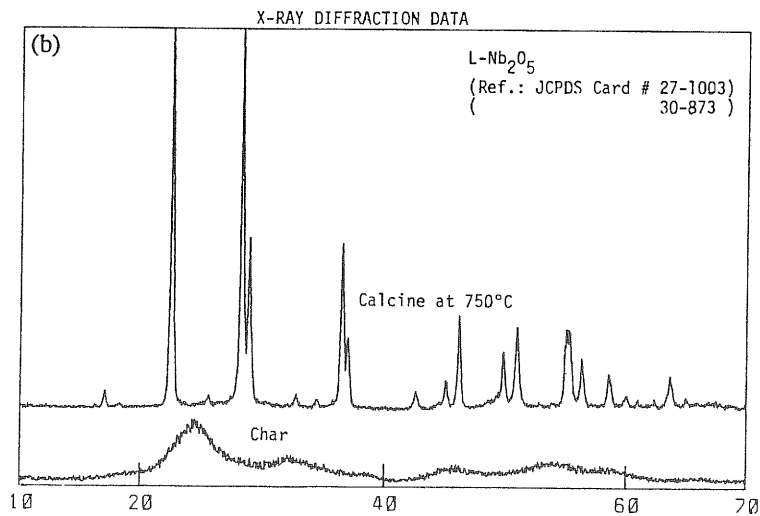


Figure 5b. X-ray diffraction pattern of Nb_2O_5 char, and powder calcined at 750°C.

3.4 Al₂O₃

Y. Sarikaya and M. Akinc [10] have prepared Al₂O₃ by emulsion evaporation of Al(NO₃)₃. They showed that stable emulsions with a broad range of Al₂(NO₃)₃ concentration can be produced at room temperature with an aqueous-to-oil phase ratio of 1:2.

We have also prepared uniform fine alumina powder from an aqueous phase of Al(NO₃)₃. Care had to be exercised during evaporation to keep NO₂ fumes and exothermic reaction problems to a minimum.

Fig. 6a shows nearly monosphere-like particles of α-Al₂O₃ after 1100°C calcining. The corresponding x-ray diffraction pattern of this powder is shown in Fig. 6b.

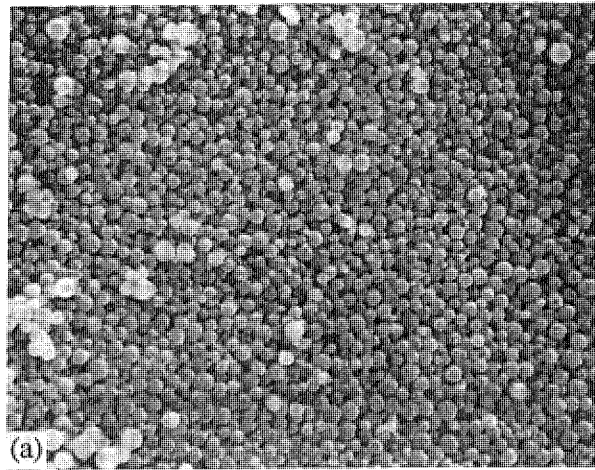


Figure 6a. Microstructure of Al₂O₃ prepared by emulsion method.
10000x Bar = 1μ

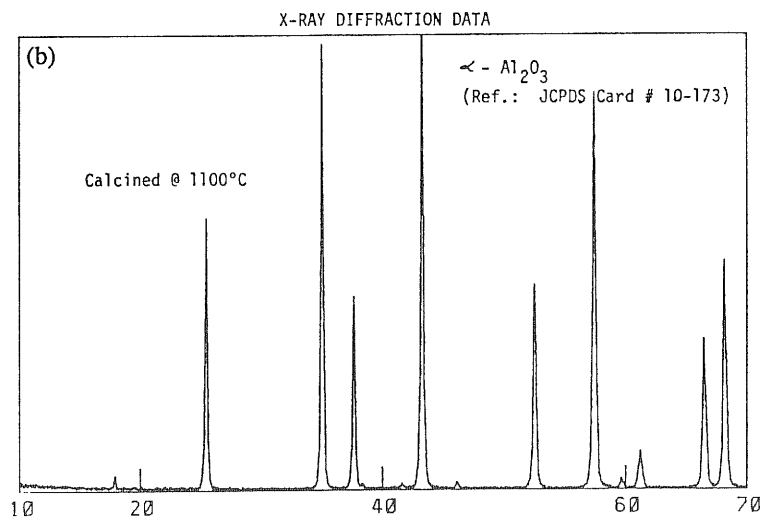


Figure 6b. X-ray diffraction pattern of Al₂O₃ powder calcined at 1100°C.

3.5 Bi₂O₃

Bismuth oxide is used as a common additive to dielectric compositions. Again, fine powders with uniform particle size are desired. However, preparation of this material by the emulsion process requires extreme care to minimize the reduction of Bi₂O₃ to bismuth metal and the maintenance of a relatively low calcining temperature (600–700°C).

Fig. 7a shows an SEM of finely divided particles in the range of 0.3 to 0.5 μm . The larger particles are mildly sintered agglomerates. Fig. 7b shows the corresponding x-ray diffraction pattern of $\alpha\text{-Bi}_2\text{O}_3$.

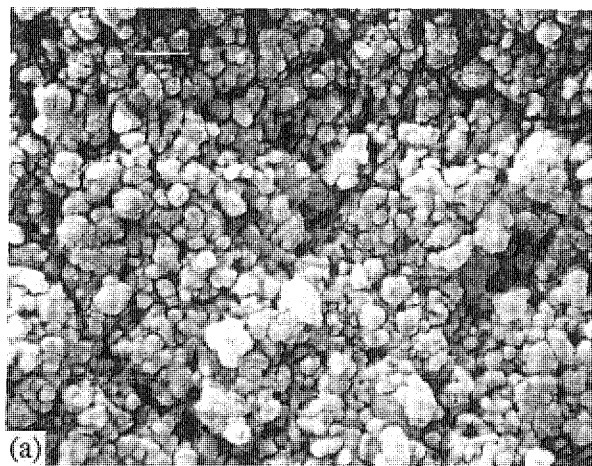


Figure 7a. Microstructure of Bi_2O_3 prepared by emulsion method.
10000x Bar = 1 μ

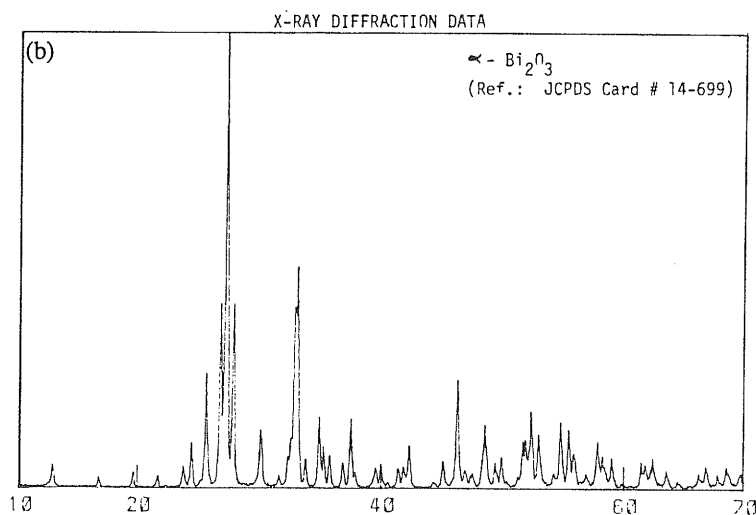


Figure 7b. X-ray diffraction pattern of Bi_2O_3 powder.

3.6 $\text{YBa}_2\text{Cu}_3\text{O}_x$ and B_2O_3 Doped $\text{YBa}_2\text{Cu}_3\text{O}_x$

High T_c super conducting (123) compounds have been prepared from an aqueous phase by the emulsion process. A small addition of B_2O_3 (<.5w%) was investigated to determine its effect on the calcining temperature. Both powders, when calcined at 550°C for 5 hours and 900°C for 5 hours, gave nearly identical properties.

Fig. 8a & 8b show the SEM of powder morphology after jet pulverizing, while Fig. 8c shows the x-ray diffraction patterns of the corresponding samples. In both cases a very small amount of BaCO_3 was detected.

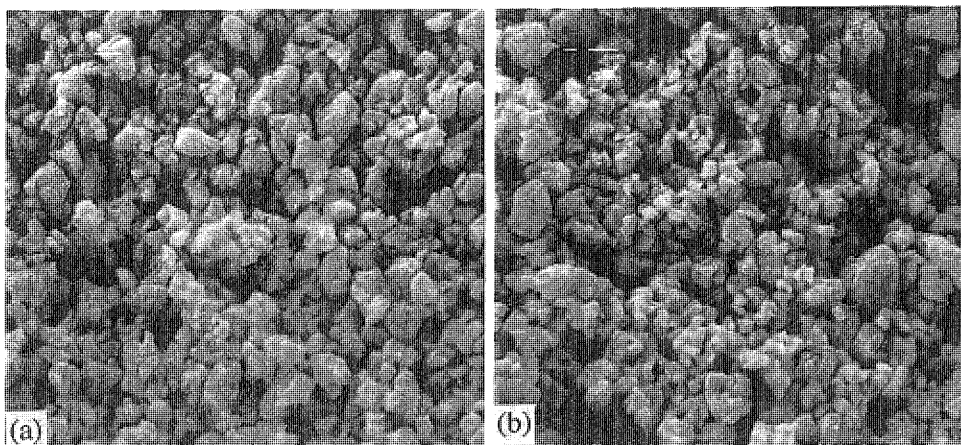


Figure 8a & 8b. Microstructure of $\text{YBa}_2\text{Cu}_3\text{O}_7$ prepared by emulsion method.

(a) Boron Doped 5000x Bar = 1μ
 (b) With out Boron 5000x Bar = 1μ

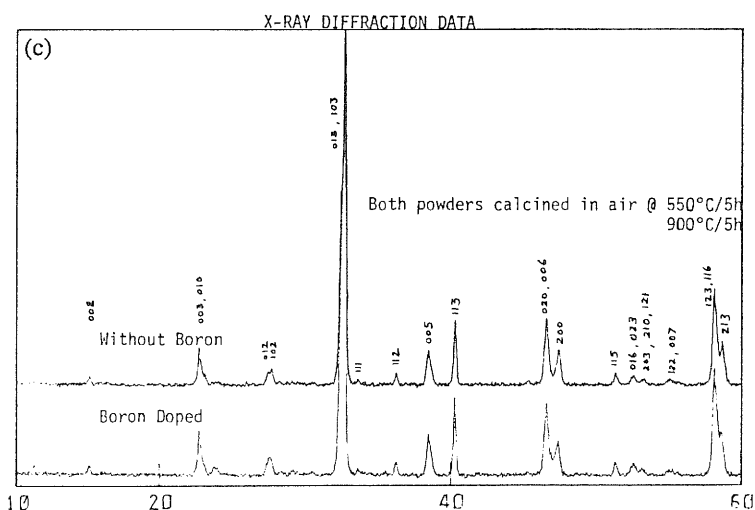


Figure 8c. X-ray diffraction pattern of $\text{YBa}_2\text{Cu}_3\text{O}_7$ with and with out Boron.

4. CONCLUSIONS

A variety of simple and complex compounds were prepared by the emulsion process. In the case of BaTiO_3 , it was possible to adjust the stoichiometry and dopant levels without significant alteration in the process. Good reproducibility was noted between small batch (300gm) and pilot scale (10Kg) preparation. Higher titanate phases were produced without major problems.

A mono-size spherical $\alpha\text{-Al}_2\text{O}_3$ was formed at 1100°C . Such a powder should be ideal for producing a fired flat and smooth surface substrate.

Additives such as Nb_2O_5 , Bi_2O_3 and Mn_2O_3 were prepared with small and uniform particle size ranging between 100 and 500nm.

The high T_c superconducting phase of $\text{YBa}_2\text{Cu}_3\text{O}_x$ prepared by this process gave similar physical properties to those reported in the literature.

Only a few of the compounds are described in this paper. Many other materials were successfully prepared, they include the following: $\text{Mg}_3\text{B}_2\text{O}_6$ and other borate compounds, BaZrO_3 , SrZrO_3 and PbZrO_3 , PLZT and PZT. Some of the properties will be described in future publications.

ACKNOWLEDGEMENTS

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