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Combustion syntheses and characterization of barium titanate, barium tetratitanate and lead substituted barium tetratitanate

Zhong, Zhimin, Ph.D.
The Ohio State University, 1994
COMBUSTION SYNTHESSES AND CHARACTERIZATION
OF BARIUM TITANATE, BARIUM TETRATITANATE
AND LEAD SUBSTITUTED BARIUM TETRATITANATE

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
Zhimin Zhong, B.S., M.S.

******

The Ohio State University
1994

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Adviser
Department of Chemistry
To My Parents
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LIST OF ABBREVIATIONS

DSC differential scanning calorimetry
DTA differential thermal analysis
DTMA derivative of thermal mechanical analysis
EGA evolved gas analysis
FTIR Fourier transform infrared
SEM scanning electron microscopy
TD thermodilatometry
TEM transmission electron microscopy
TG thermogravimetry
TG/DTA simultaneous thermogravimetry and differential thermal analysis
TMA thermal mechanical analysis
XRD X-ray diffraction
CHAPTER I

Introduction

1.1. BaTiO$_3$ and BaTi$_4$O$_9$

Eight compounds have been found in the BaO-TiO$_2$ system. They are Ba$_2$TiO$_4$, BaTiO$_3$, BaTi$_2$O$_5$, Ba$_6$Ti$_{17}$O$_{40}$, Ba$_4$Ti$_{13}$O$_{30}$, BaTi$_4$O$_9$, Ba$_2$Ti$_6$O$_{20}$ and BaTi$_5$O$_{11}$. The general formula for these compounds is Ba$_x$Ti$_y$O$_{x+2y}$. They are of great technical interest because of their ferroelectric properties. BaTiO$_3$, in particular, has been widely used in the manufacture of multilayer capacitors, thermistors and electro-optic devices. BaTi$_4$O$_9$ is a microwave resonator, which has found application in microwave technology and wireless communications such as cellular phones.

Barium titanate (BaTiO$_3$) is the textbook ferroelectric material with well defined polarization, low temperature phase transition and commercially useful high dielectric constant. BaTiO$_3$ exists in
various crystal structures as a function of temperature. It has a rhombohedral crystal structure below -90°C, orthorhombic between -90 and 0°C, tetragonal between 0 and 120°C, cubic from 120 to 1460°C, and hexagonal from there until it melts at 1618°C.\(^3,5\)

![Image of crystal structures]

Figure 1.1 Perovskite Structure for BaTiO\(_3\)

The cubic BaTiO\(_3\) assumes the Perovskite structure, isostructural with the mineral perovskite (CaTiO\(_3\)).\(^2,3,5\) Many useful ferroelectric ceramics, such as PbTiO\(_3\), PbZr\(_x\)Ti\(_{1-x}\)O\(_3\), KNbO\(_3\), also have the
Perovskite structure. Figure 1.1 is the structure of cubic BaTiO$_3$.

There are twelve nearest-neighbor oxide ions around every barium ion; and six oxide ions around every titanium ion in octahedral coordination. The barium and oxide ions together form a cubic close-packed array with titanium ion filling those octahedral holes formed exclusively by oxide ions.

The cubic structure transforms on cooling to a tetragonal structure at 120°C, with contraction of two edge lengths and expansion of the third. The ratio of edge lengths (c/a) is about 1.01. The enthalpy of the phase transition is -0.201 kJ/mol. The phase transition distorts the oxide octahedron and therefore shifts the minimum-energy positions for the titanium ion; the positions are off center after the transition. That in turn changes the minimum-energy positions of every ions. The ion positions in tetragonal BaTiO$_3$ have been measured by single crystal x-ray diffraction and neutron diffraction. Figure 1.2 shows the relative displacements of ions in a unit cell. The displacements split the centers of positive charge and negative charge in a unit cell and causes spontaneous polarization in a crystal, therefore
the crystal becomes polar. Crystals that exhibit a spontaneous polarization are called ferroelectric crystals. Ferroelectricity is defined as the spontaneous alignment of electric dipoles by their mutual interaction.

Figure 1.2 Position Shifts in Tetragonal BaTiO₃

In contrast, crystals that do not exhibit a spontaneous polarization are known as paraelectric crystals. Some crystals are ferroelectric in a certain temperature range and the phase transition temperature between
ferroelectric and paraelectric crystal is known as Curie point. \( \text{BaTiO}_3 \) has a Curie point of 120°C. Both rhombohedral and orthorhombic \( \text{BaTiO}_3 \) are ferroelectric, so the two low temperature phase transition points are not Curie temperatures. Usually, uniform alignment of electric dipoles only happen in some regions of a crystal, and the spontaneous polarization may be in a different direction in other regions. The regions with uniform polarization are called ferroelectric domains. The direction of spontaneous polarization can be reversed by an external electric field.

\( \text{BaTiO}_3 \) based materials have been used in ceramic capacitors for more than forty years due to their high dielectric constant (permittivity).\(^3\)\(^5\) The very high dielectric constant makes it possible to achieve high capacitance with very small size. That is an important factor for the advancement of microelectric circuit. Further improving the performance of the ceramic capacitors depends on better processing of the material.

Another important application for \( \text{BaTiO}_3 \) is as a temperature controlling devices.\(^3\) Pure \( \text{BaTiO}_3 \) ceramic is an insulator. It turns into
a semiconductor with the substitution of 0.1-0.3 molar percent rare earth elements such as La, Sm and Ce for the Ba. These semiconducting BaTiO$_3$ (doped) show a very high positive temperature coefficient of resistivity in the region of the tetragonal to cubic phase transition. The increases in resistivity are four to six orders of magnitude.$^3$ This feature makes them useful materials as thermistors by inserting them into an area where the temperature must be controlled.

BaTiO$_3$, PbTiO$_3$ and SrTiO$_3$ form continuous solid solutions of Ba$_x$Sr$_{1-x}$TiO$_3$ and Ba$_x$Pb$_{1-x}$TiO$_3$ with Curie points that range from -220 to 490°C. The solid solutions doped with the rare earth elements have the same semiconducting properties as that of BaTiO$_3$ and can be used for controlling the temperature in the temperature range near their Curie points. Doped and multicomponent BaTiO$_3$-based ceramics also find application in electro-optic devices.$^3$

The high dielectric constant of BaTiO$_3$ in the frequency range of particular interest for the specific electric circuit permits miniaturization of the components and therefore of the circuits themselves. As example, the high dielectric constant of barium
tetratitanate (BaTi$_4$O$_9$) and related materials in the microwave frequency range is the basis of miniaturization of the microwave resonator. This makes contemporary cellular phones possible. BaTi$_4$O$_9$ has an orthorhombic crystal structure with two molecules of BaTi$_4$O$_9$ in each unit cell.$^7$ The structure is the same as that of KTi$_3$NbO$_9$.$^8$ Figure 1.3 depicts the structure of BaTi$_4$O$_9$. It shows zigzag ribbons of TiO$_6^{4-}$ octahedra sharing edges and corners. There is no face-sharing of TiO$_6^{4-}$ octahedra. Ba$^{2+}$ ions are in between the octahedron matrices. The octahedra are somewhat distorted. Therefore, Ti$^{4+}$ ions are not in the center of octahedra similar to the tetragonal form of BaTiO$_3$.

Figure 1.3 Structure of BaTi$_4$O$_9$ Viewed from One Axis
1.2. Existing Synthetic Methods for BaTiO$_3$ and BaTi$_4$O$_9$

The way we utilize materials for technological development is an important indicator of human progress and civilization. Contemporary microelectronic technology that is vital to our daily life hinges on many metal oxide based ceramic materials that have appropriate electrical and magnetic properties. Ceramic materials are conventionally prepared by solid-state reactions between their compositional metal oxides and/or carbonates. For electronic application, solid-state reactions generally tend to produce less than optimum materials. This limits performance and miniaturization of electronic devices in many cases. As a result, new processing procedures that will generate high quality materials are of great technological importance. The potential higher costs of the processes are justified by significantly improved properties, performance, and devices.

None of the compounds in the BaO-TiO$_2$ system exists in nature. BaTiO$_3$ was independently synthesized by different people in the United States, Japan and the former Soviet Union around 1943.$^3$ Most
of the compounds were first synthesized by solid-state reactions between appropriate ratios of BaCO₃ and TiO₂.

The traditional synthesis of BaTiO₃ starts with weighing and ball milling TiO₂ and BaCO₃.³⁹,¹⁰ The mixtures are calcined at high temperatures (1100-1250°C). Because the rate-limiting step in solid-state reaction is the diffusion of atoms or ions between different phases, high temperatures and long reaction times are required. Repetitive calcination and grinding treatments are necessary to synthesize single phase product because there are several compounds in the BaO-TiO₂ system. Defect structure induced by poor local stoichiometry tends to exist due to different diffusion rates for the ions.¹⁰

Synthesis of BaTi₄O₉ by solid-state reaction was reported as early as 1951.¹¹,¹² The crystal structure was resolved later.⁷ Low temperature synthesis for the compound is still not as accessible as BaTiO₃. As a result, solid-state reaction between BaCO₃ and TiO₂ is still a popular method to prepare BaTi₄O₉.¹³ As high purity BaTiO₃ is relatively easy to make (this will be discussed later in this section), the solid-state reaction between BaTiO₃ and TiO₂ to prepare BaTi₄O₉ is the other
option.\textsuperscript{4,14} The standard sample for powder X-ray diffraction used by NIST was made by the latter method. BaTiO\textsubscript{3} and TiO\textsubscript{2} were mixed by grinding with acetone in a 1:3 molar ratio. The calcination and grinding steps included: 800\textdegree{}C for 20 hours and grinding; 1175\textdegree{}C for 25 hours and grinding; 1250\textdegree{}C for 20 hours and grinding; and 1325\textdegree{}C for 4 days.\textsuperscript{14}

Two major steps to produce ceramic parts and devices are powder processing and sintering. The prepared powders are formed, usually by pressing and sintering into articles having the appropriate shape and mechanical strength. Fine powders are, in general, preferred for the processing of ceramic materials as they tend to sinter better and more readily.\textsuperscript{3,15} Particle size always increases during sintering. On the other hand, pure BaTiO\textsubscript{3} pellets exhibit the highest dielectric constant in samples where the average grain size is about 1 \(\mu\text{m}\) and that have very high sintered density.\textsuperscript{16} Impurities such as alumina, silica, phosphorus etc. are known to have detrimental effects on the electronic and mechanical properties of BaTiO\textsubscript{3} and BaTi\textsubscript{4}O\textsubscript{9}.\textsuperscript{4,17} High temperature during the solid-state reaction is the cause of coarse
particle size. Ball milling and grinding always introduces milling media such as alumina, silica and/or zirconia as impurities. As a result, BaTiO₃ powder made by solid-state reaction tends to be coarse, impure and inhomogeneous powder, always having less than optimal properties.

High purity, homogeneous and submicron powder of BaTiO₃ has been synthesized by many low temperature, wet chemical routes such as coprecipitation, hydrothermal, sol-gel, freeze drying techniques etc.¹⁷ New synthetic methods are frequently reported.¹⁸,¹⁹,²⁰ One common approach in these procedures is to provide better contact (shorter diffusion paths) between Ba and Ti and therefore high temperature diffusion is minimized. Coprecipitation is a very successful method that has been used to prepare commercial high purity BaTiO₃. If a complex compound can form between Ba and Ti with a 1:1 atomic ratio, then the Ba and Ti are mixed at the atomic level and may convert to BaTiO₃ without the diffusion step. BaTiO(C₂O₄)₂·4(~5)H₂O is a well known coprecipitate which is a molecular precursor for BaTiO₃.¹⁷,²¹-²³ The procedure for precipitating BaTiO(C₂O₄)₂·4(~5)H₂O and then
converting it to $\text{BaTiO}_3$ by calcination in air around $950^\circ \text{C}$ is known as the "oxalate process". It is now used commercially to prepare high quality $\text{BaTiO}_3$. Besides oxalic acid, citric acid, tartaric acid and catechol are also good coprecipitate agents for preparing $\text{BaTiO}_3$.\textsuperscript{17,24}

Fluxing and hydrothermal approaches are effective ways for better contact between reactants in the synthesis of crystalline products.\textsuperscript{25} Fluxing is the method of choice to prepare single crystal $\text{BaTiO}_3$.\textsuperscript{3} $\text{BaTiO}_3$ fine powder and thin films get more attention because of their extensive applications. The reactants of barium and titanium in hydrothermal synthesis are soluble barium salts or hydroxide and $\text{TiO}_2$ or a gel of hydroxide titanium.\textsuperscript{17,26} The reactants are heated from 85 to $500^\circ \text{C}$ for long times in a basic aqueous environment. The reaction is carried out in a closed vessel to accommodate high pressure. The kinetics of the reaction favors the formation of $\text{BaTiO}_3$ at much low temperature than in solid-state reaction. A hydrothermal technique was first used to synthesize submicron $\text{BaTiO}_3$ powder\textsuperscript{17}. It has been used to synthesize $\text{BaTiO}_3$ powder with desired particle size by controlling the anion of barium
salt along with the reaction time and temperature. A layer of titanium oxide can be formed on a titanium plate by oxidizing the plate, the hydrothermal method can then be utilized to synthesize a BaTiO$_3$ thin film on the titanium plate.\textsuperscript{26b}

Coprecipitation of a unique precursor and hydrothermal techniques apply to the synthesis BaTiO$_3$ only. All coprecipitated precursor compounds that have been found are 1:1 for Ba and Ti.\textsuperscript{17} BaTiO$_3$ with highest purity has been prepared by the simultaneous hydrolysis of alkoxides of barium and titanium in an alcoholic solution.\textsuperscript{1,17} The organometallic reagents can be easily purified, therefore, levels of most impurity in BaTiO$_3$ prepared by this method are minimized. The reagents are sensitive to moisture and carbon dioxide, thus the experimental procedures are conducted in an argon atmosphere. So, the preparation method suffers from high costs of reagent materials and the necessary operations. Crystalline BaTiO$_3$ having a particle size of 5-10 nm was formed upon hydrolysis of equimolar mixed barium and titanium ethoxide solutions.\textsuperscript{1} High purity
BaTiO₃ was obtained by heating the initial BaTiO₃ to remove absorbed organic solvent.

As the process starts with all reactants in a solution, it can be carried out for the synthesis of other compounds in the BaO-TiO₂ system by mixing alkoxides of barium and titanium in the appropriate ratios.¹ When the method was applied to BaTi₄O₉, a single phase product was not obtained until the hydrolytic mixed precipitate was heated to 1300°C.¹ By using different alkoxide reagents, BaTi₄O₉ has been prepared by heating the hydrolytic mixture at 1100°C for three hours.²⁷ Therefore, it is not a good method for preparing fine powder BaTi₄O₉. On the other hand, it is a generally useful synthetic tool and pure BaTi₅O₁₁ was first synthesized by this method.¹

The sol-gel technique is an important current method for processing ceramics, glass and their thin films.²⁸ The sol-gel method has also been applied to synthesis of BaTiO₃.¹⁷,²⁹,³⁰ Though the solvents and synthetic conditions used by each investigators were different, the overall approach was very similar. In all cases, titanium isopropoxide, barium acetate, acetic acid, alcohol and water were mixed appropriately
to avoid quick hydrolysis. Titanium isopropoxide is not very sensitive
to water and carbon dioxide, so the processing can be performed in air.
Acetic acid is there to prevent fast hydrolysis. The mixture was stirred,
either at room temperature or elevated temperature, to allow formation
of the sol. The liquids in the mixture were allowed to evaporate, and a
gel formed as the residue. The drying always took several days. The
gel was further dried around 100°C. In all cases, the xerogel (dried
gel) was amorphous and contained about 50 % by weight of organic
residues, which must be heated to above 900°C to get pure
BaTiO$_3$.\textsuperscript{17,29,30}

As sol-gel processing starts from mixing solutions of several
reagents in any ratio to form a homogeneous sol, one advantage of the
technique is its applicable to the other compounds in the BaO-TiO$_2$
system. It has been applied to synthesize Ba$_2$TiO$_4$, BaTi$_2$O$_5$ and
BaTi$_4$O$_9$ as well as BaTiO$_3$.\textsuperscript{30} Again, the xerogel must be calcined to
get the desired product. Sol-gel processing is the only procedure ever
reported to synthesize BaTi$_4$O$_9$ below 1000°C.
A frequently-vaunted advantage of the sol-gel technique is its high homogeneity during the step to step processing. It does not apply to BaTiO$_3$ well because XRD patterns for gel powders calcined at various temperature showed the formation of BaCO$_3$ "islands" around 500° C.$^{17,29}$ The processing also suffers from long processing time and consumption of large amount of organic compounds. A commercial material for sol-gel processing of BaTiO$_3$ is BaTi(C$_7$H$_{15}$COO)(i-C$_3$H$_7$O)$_5$ (barium titanium ethylhexanoate-isopropoxide) in isopropanol (Chemat Technology, Inc., Northridge, CA) has been available. It can be used for BaTiO$_3$ thin films or bulk ceramics.

1.3. Combustion Synthesis

Synthesis of new materials and processing materials into a useful form, such as thin films, are generally tied to new processing methods.$^{25,31}$ This is because many useful materials are not in their most stable phase. Solid-state reactions which rely on high temperature diffusion usually generate thermodynamically most stable phase at that temperature. Therefore, it cannot be used to prepare compounds that
are stable at low temperature but decompose at high temperature. Important metastable materials include BaTi$_5$O$_{11}$ and many high-T$_c$ superconductors.$^{1,25,31,32}$

New processing techniques strive for more cost-effective approaches. So, there is tremendous interest to develop new processing methods and to apply existing methods to new systems. Combustion synthesis is a promising technique for the processing of material.

Combustion synthesis is also known as self-propagating high-temperature synthesis$^{33,34}$ and the anionic oxidation-reduction method.$^{35}$ The technique was initiated by researchers in the former Soviet Union around 1967.$^{33}$ The name of the method implies a high temperature processing. It is a combustion process of any chemical nature that results in the formation of valuable solid product. The process starts with intimately mixing selected reactants so that the reaction will proceed in a self-contained way. The chemical reaction of the process is a highly exothermic one. It is a thermal runaway, of explosive character sometimes. For a long time, the research was focused on syntheses of intermetallics, carbides, borides, silicides, nitrides etc.
with solid-solid reactions and solid-gas reactions. The method has been applied to synthesize a high-$T_c$ superconductor by the reaction,

$$3\text{Cu} + 2\text{BaO}_2 + \frac{1}{2} \text{Y}_2\text{O}_3 + \frac{3}{4} \text{O}_2 \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_7.$$  \hspace{1cm} (1)

Combustion synthesis is similar to the magnesium thermite process and aluminum thermite process in the reaction aspect. A distinct difference is that the thermite process always has an undesired solid by-product. Combustion synthesis should not have one.

Wet chemical methods have not been introduced into combustion synthesis until very recently. The combined technique has been focused on processing ceramics such as high-$T_c$ superconductors, $\alpha$-aluminas, dielectric materials, spinel ferrites, and more complicated ceramics such as $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Zr}_4\text{P}_6\text{O}_{24}$ for thermal shock resistance. Since the chemical reaction of the method proceeds very quickly, the traditional calcining effect is very limited. Actually, it has been used to prepare metastable materials that conventional solid-state reactions could not. (see Chapter 4)

Many advantages of combustion synthesis have been discussed. On the processing side, the method needs little initial heating to start a
fast reaction and requires little or no further calcination. Therefore, there is big saving of time, energy and heating equipment. On the product side, the method can be used to produce new metastable products that conventional solid-state reaction and other synthetic methods cannot. The products of combustion synthesis are always in ultrafine powder form and therefore have good sinterability.

Combustion is an oxidation-reduction reaction. Oxidizing agents and reducing agents for the reaction are mixed appropriately to ensure that the reaction proceeding in a self-propagating manner. Several ways to carry out the reaction have been reported. One way was to mix solid reactants in an agate mortar by adding small amount of water, then the homogeneous slurry was transferred to a container and heated in a furnace.\(^{36,39}\) Sometime a mixed solution was heated in a furnace directly.\(^{19,37}\) A highly exothermic reaction would generate the desired product. Phase segregation happened when the reactants were not so well-mixed.\(^{19}\) Another way was to spray dry a mixed solution of parts of reactants (i.e. nitrates of iron and copper).\(^{38}\) Then the spray dried product, as the oxidizing reagent, was mechanical mixed with cellulose
powder as a reducing reagent. This mixture was then heated to complete the processing. Phase segregation was also observed.38

If all the reactants are soluble, spray drying a solution that contains all the reactants will provide a better mixed state between reactants, and therefore generate a more homogeneous product.35 YBa2Cu3O7 and YBa2Cu4O8 have been prepared by spray drying aqueous solutions (in subsequent text, solution always means an aqueous solution) of appropriate salts. The best processing conditions were achieved by varying the ratios of acetate (or other reducing anions) to nitrate while keeping the cation ratios for the desired products (1:2:3 of Y:Ba:Cu for YBa2Cu3O7 and 1:2:4 of Y:Ba:Cu for YBa2Cu4O8). The optimum ratio of anions was determined when differential scanning calorimetry (DSC) of the spray dried product indicated a single highly exothermic reaction. The thermal decomposition of these spray dried mixtures can occur at a relatively low temperature initiating a self-contained oxidation-reduction process. The actual temperature that the reaction achieves is determined by the extent of the thermal runaway process and is also affected by the
thermal environment. The temperature can be measured by optical pyrometer. In all cases herein, the exothermic reactions began below 300°C.

The procedure starts with all chemical components in a solution. As a result, various ratios between the components can be in the solution and subsequently spray dried into an intimately mixed state. Spray drying is an important means to convert a solution to a relatively uniform solid. It involves the atomization of a solution into droplets which are dried to individual particles upon contact with hot air. The procedure was called the "anionic oxidation-reduction method" by Kourtakis et al. Actually, it fits into combustion synthesis. Freeze drying would be a viable alternative to spray drying. In the following text, application of the procedure to the syntheses of BaTiO₃, BaTi₄O₉ and PbₓBa₧₋ₓTi₄O₉ (where x is 0.1, 0.2 or 0.5) will be discussed. The powders prepared have been characterized by various means and selected properties will be described.
CHAPTER II

Combustion Syntheses of

BaTiO₃, BaTi₄O₉ and PbₓBa₁₋ₓTi₄O₉

2.1. Review of Low Temperature Approaches

High purity, homogeneous and ultrafine BaTiO₃ powder has been prepared by many low temperature, wet chemical routes. The oxalate process has been commercial used to prepare high quality BaTiO₃. Sol-gel method has been successfully applied to synthesize BaTiO₃, BaTi₄O₉ and other compounds in the BaO-TiO₂ system.

Detrimental effects of impurities such as alumina, silica and phosphorus are well documented. On the other hand, pure BaTiO₃ as electric capacitor material has a poor (very high) temperature coefficient.⁵,⁴⁰ Dopants and substitutes will not only reduce its temperature coefficient dramatically, but also increase the dielectric constant significantly. Actually, pure BaTiO₃ is rarely used in ceramic
capacitor without compositional modifications. Semiconducting BaTiO₃ for thermistor application is also a doped ceramic. As a result, new synthetic approaches that can easily and homogeneously introduce dopants and substitutions are of great interest.

The oxalate process which has successfully produced high purity BaTiO₃ has some difficulty to introduce dopants and substitutions. This is because the stoichiometry of the oxalate coprecipitate is limited to 1:1 for barium and titanium. When Ba is replaced by Sr, Pb and etc., these ions in the starting solution cannot perfectly coprecipitate. For thermistor application, high purity BaTiO₃ is prepared by the oxalate process at first, then the dopants and substitutes are introduced by high temperature calcination (solid-state reaction). So the processing is only partially low temperature. A complete low temperature method will generate the devices with various grain size, which may optimize those devices further.

Sol-gel processing provides a homogeneous procedure from a liquid-mix to a solid product. The first low-temperature route for the synthesis of BaTi₄O₉ was achieved by this technique. The ability to
introduce dopants and substitutes in sol-gel processing has not been investigated. It is probable that some dopants and substitutes will segregate in some manner such as precipitate either before or after other components. This would make high temperature calcination necessary to get homogeneous product. Besides, sol-gel processing suffers from long processing times and high costs of organic solvent and organic metallic reagents.

The combustion synthesis for high-\text{T}_c\ superconductor\textsuperscript{35} provides an excellent alternative to meet these challenges. The technique should be able to apply to the synthesis of doped and multicomponent BaTiO\textsubscript{3}-based powders and BaTi\textsubscript{4}O\textsubscript{9}-based powders directly. The cost of the processing is reasonable and the product will be very homogeneous. Therefore, there is a good commercial potential.

2.2. Aerosol Drying, Freeze Drying and Spray Drying

Aerosol drying, freeze drying and spray drying are three major means to convert a solution to a relatively uniform solid. The mechanism and the application of the dryings will be briefly discussed.
Aerosol is a colloidal suspension of particles in a gas. The aerosol exists in nature as a fog if the particles are liquid and a smoke if the particles are solid. The particle size of aerosol (or colloid) is between one nm to one μm. It is so small that gravitational forces are insignificant and the particles exhibit Brownian motion. A solution is transformed to aerosol form in the method by focusing an ultrasonic beam on the surface of the solution. Ultrafine droplets of the solution are produced above the surface. The ultrafine droplets are then carried away by a purge gas as an aerosol. The aerosol is dried to ultrafine powders by being passed through a furnace in the drying.

Spray droplets generated by nozzle have a wide dispersion of droplet size. A technology has been developed to remove the large droplets from the spray generated by collision-type nozzles. The droplet sizes of the remaining were between 0.1 to 1.0 μm. One shortcoming with this method is that only a very small portion of solution will convert to aerosol form in one cycle.

As solution droplets in aerosol are very small, extremely homogeneous powder can be prepared by this drying technique since
any segregation during drying is restricted to the individual droplet. On the other hand, there are about two milligrams solution in a cubic meter aerosol. Only a few grams of dried powder can be prepared in one hour, even by using a large scale aerosol generator. Therefore, the cost of the drying is very high.

Freeze drying is a relatively expensive form of industrial drying. Nevertheless, it is used on a large scale in the food, biological and pharmaceutical industries. The uniqueness in the drying is its low temperature. Therefore, this method of drying is very valuable for substances that are heat sensitive. The solution is initially frozen by exposure to very cold air or immiscible fluid. The water is removed as a vapor by sublimation from the frozen solution in a vacuum chamber below the triple point temperature of water.

Spray drying transforms a solution into a dried product in a single, continuous step. The solution is atomized using a rotary atomizer or a nozzle, and the spray of the solution droplets comes immediately in contact with a flow of hot drying air. The resulting rapid evaporation maintains a low droplet temperature so that high
drying air temperature can be applied without affecting the product too much. As the time of drying is very short, phase segregation among the components in the solution is minimized and restricted to the droplet's dimension.

Atomization is a process with a dramatic surface area increase for a solution. It takes a lot of energy. There are three types of atomizers for spray drying, each provide energy in a different way. Rotary atomizers provide centrifugal energy through a high-speed spinning wheel. Liquid is fed into the center of a turning wheel, moves to the edge and is divided at the edge into droplets. Pressure nozzles provide pressure energy and two-fluid (pneumatic) nozzles provide kinetic energy for the process. In two-fluid nozzles, compressed air is used to atomize the solution. The two-fluid nozzle spray dryers have the lowest energy efficiency among the three. Most mini spray dryers for laboratories are two-fluid nozzle type. They are very flexible, need little accessory and are without moving parts.

The sizes of droplets are dependant on types of spray dryers and the operating conditions. Usually, there is a wide distribution from a
few \( \mu m \) to a few hundred \( \mu m \), which is much larger than that of aerosol. The feed rate for an industrial spray dryer (rotary atomizer type) can be up to 200 tons per hour (Niro Inc., Columbia, MD).

Besides solutions, spray drying can be applied to any pumpable fluid such as emulsion and slurry. It is used to dry pharmaceutical fine chemicals, foods, dairy products, blood plasma, ceramic powders and polymer product.\(^4\) It also finds application in processing advanced ceramics such as carbides, nitrides and a variety of composites with new formulations.\(^5\)

2.3. The Spray Dryer for the Research

The spray dryer used for this work is a Büchi 190 mini spray dryer (Brinkmann Instruments Inc., Westbury, N.Y.). It is a two-fluid nozzle type. Figure 2.1 is the diagram of the spray dryer. This spray dryer weighs about 71 kilograms and occupies only 0.5 square meter bench space. It can dry up to 1.5 kilograms solution per hour. The temperature of hot air (inlet temperature) can reach 220\(^\circ\)C. A cyclone
1 Air intake
2 Heating
3 Flow stabilized entrance into the drying chamber
4 Cyclone separates the product from the air stream
5 Aspirator
6 Temperature sensor «air inlet». This temperature is regulated by the heater.
7 Temperature sensor «air outlet». The optimum selection of the temperature difference between the «inlet» and «outlet» temperatures is one of the most important aspects of spray drying. The outlet temperature cannot be set as desired since it results from a combination between the inlet temperature - aspirator setting and product-feed pump performance.
8 Receiving vessel for the final product

A Solution, emulsion or dispersion of the product
B Peristaltic feed pump
C Product channel
D Connection for spray flow (pressurized air or inert gas).
E Connection for cooling water
F Nozzle needle with twist channel
   The needle can be used to clear the nozzle should it become clogged by the product. For difficult products, the nozzle needle can be operated automatically. This device is available as an accessory.

Figure 2.1 Mini Spray Dryer for this Work
Separator is used to separate the dried product from the exhaust air that contains a lot of moisture during the operation.

When the solutions for the combustion synthesis were spray dried, the inlet temperature was controlled at about 160°C. This is because the dried powders are very reactive and a higher temperature may start a runaway reaction. Consequently, the pump rate was maintained at approximately 200 ml of solution per hour to guarantee a good drying process. The temperature prior to the cyclone (outlet temperature) was about 75°C.

2.4. Preparation of Titanyl Nitrate, TiO(NO₃)₂, and the Determination of its Concentration

All reactants for the combustion synthesis must be soluble. Anions for the salts as reactants should decompose easily upon heating. The anions good for the processing are nitrate and organic anions such as acetate. Chloride and sulphate should be avoided as they will remain in the product as impurity after the combustion processing. Soluble titanium(IV) simple salts include TiOCl₂, TiOSO₄ and TiO(NO₃)₂.
These compounds only exist in strongly acid media and will hydrolyze otherwise.\textsuperscript{2,46} TiO(NO\textsubscript{3})\textsubscript{2}, which is the source of titanium for manufacturing PbZr\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{3},\textsuperscript{3,46} was chosen as the source of titanium for the combustion syntheses. It also has been used for BaTiO\textsubscript{3} syntheses by other investigators.\textsuperscript{19,47}

Titanyl nitrate is not commercially available and was prepared in the laboratory.\textsuperscript{46} A very similar synthesis has been used by other investigators.\textsuperscript{19,47} There were some small modifications here. Instead of adding titanium tetrachloride (TiCl\textsubscript{4}) to dilute hydrochloric acid,\textsuperscript{46} TiOCl\textsubscript{2} was prepared by slowly adding about 10 ml TiCl\textsubscript{4} to 50 ml deionized water which was cooled in an ice bath.\textsuperscript{21,22} The clear solution was then mixed with 1 liter 1.5 M ammonium hydroxide solution, which precipitated hydrated titanium oxide as a fluffy slurry. The slurry was washed by deionized water till the decantation was free of chloride ion (tested by mixing with a silver nitrate solution).

The hydrated titanium oxide slurry collected on filter paper was between 60-70 ml. It contained a lot of water which was then blended with 120-140 ml of 1.4 M nitric acid. A minimum amount of nitric
acid was used to dissolve hydrated titanium oxide to avoid waste. The mixture was stirred on an ice bath till almost all of the slurry was dissolved. A small amount of insoluble residue was removed by filtering the solution. The titanyl nitrate solution is known to be unstable with respect to hydrolysis. The clear solution was found stable in room temperature for a few days and it can be stored in a refrigerator for more than three months. The solution was free of chloride ions. Hydrogen peroxide can stabilize the solution, which also creates an intense orange colored solution. Since the chilled filtered solution was reasonably stable, several batches of TiO(NO$_3$)$_2$ solution were combined in a one liter plastic bottle for storage.

High purity TiCl$_4$ (Aldrich, 99.9%) was used for the preparation. It seems that hydrated titanium oxide can be obtained by adding TiCl$_4$ to ammonium hydroxide solution directly. The hydrated titanium oxide made this way was hard to dissolved in nitric acid and chloride ion in the slurry was difficult to wash away. TiO(NO$_3$)$_2$ cannot be prepared by dissolving titanium oxide (TiO$_2$) in nitric acid.$^2$
The concentration of TiO(NO₃)₂ in the solution was determined by gravimetric analysis.¹⁹,⁴⁷ About 10.0 ml of the solution was taken by a pipette to a platinum crucible. The weight of the solution was measured by an analytical balance. Then the crucible containing the 10.0 ml of solution was heated slowly on a hotplate till most of the water was evaporated. The crucible was fired on a Bunsen burner to convert the residue of the solution to TiO₂. The concentration of TiO(NO₃)₂ in the solution was calculated based on the weight of the TiO₂. Two determinations were always performed on the same solution as a check. The concentration was expressed in moles of titanium in 1000 grams of the solution. When the TiO(NO₃)₂ solution was mixed with other solutions, it was weighed to determine the moles of titanium for stoichiometry. Odd amounts of solutions can be delivered much more accurately by weight than by volume. Excess nitric acid was in the solution, which also deterred hydrolysis. The total acid concentration including TiO²⁺, which was equal to NO₃⁻ concentration, was determined by a titration with standard base.
There was about 10% variation between the concentrations of TiO(NO₃)₂ in the solution from batch to batch. The concentration in one batch was 0.21154 moles titanium per kilogram solution. This was similar to the 10 grams titanium per liter by an earlier investigator. The total NO₃⁻ concentration in the solution was about 1.0 M.

2.5. Selection of Reducing Compounds for the Combustion Synthesis of BaTiO₃

The thermal decomposition of the spray dried product was determined by thermal analysis. Simultaneous thermogravimetry and differential thermal analysis (TG/DTA) was performed using a Seiko TG/DTA 320 module of a SSC/5200 system. The spray dried products were put in an open platinum sample pan. The sample pan together with an empty reference pan were heated at 10°C/min from room temperature to 1000°C. Air at 100 ml/min was used as purge gas. Such a run will reveal all thermal events associated with enthalpy and weight changes when the sample is subject to that temperature program.
The attempt to mix nitrate with acetate for the combustion synthesis failed. The TG/DTA curve of the spray dried product of 1:1 molar ratio of TiO(NO₃)₂ and Ba(CH₃COO)₂ showed no exothermic peak. It exhibited a major endothermic peak associated with weight loss around 580°C, which corresponded to the melting/decomposition of Ba(NO₃)₂. The reason is probably the volatility of acetic acid during the spray drying process and lower solubility of Ba(NO₃)₂ converted Ba(CH₃COO)₂ to Ba(NO₃)₂. BaTiO₃ was obtained by calcination the spray dried product at 700°C for an hour. Without a reducing component, there is no highly exothermic decomposition and a multistage reaction involving phase segregation is unavoidable.

Glacial acetic acid was added in the solution to help precipitate acetate during the spray drying. When excess glacial acetic acid was added, a precipitate of Ba(NO₃)₂ appeared based on its XRD and TG/DTA tests, which further exhibited the disparity in solubility between Ba(CH₃COO)₂ and Ba(NO₃)₂. The spray dried product of the solution with a maximum amount of glacial acetatic acid only contained a small amount of acetate. Figure 2.2 is the TG/TDA curve
Figure 2.2 TG/DTA for 1:1 BaAc$_2$, TiO(NO$_3$)$_2$ with glacial HAc
of such a spray dried product, which shows a major endothermic peak around 580°C with a small exothermic peak around 350°C.

In subsequent work for the combustion synthesis in the BaO-TiO₂ system, Ba(NO₃)₂ (Aldrich, 99.98%) was used as the source of barium because it is less expensive for a pure source of barium.

Oxalic dihydrazide (C₂H₆N₄O₂) and tetraformal triazine (C₄H₁₆N₆O₂) are two hydrazine (N₂H₄) derivatives that have been used as reducing components in the combustion syntheses for spinel ferrites and dielectric oxide ceramics. The reactions between them and many nitrate salts were known to be violent, of a combustive nature. TG/DTA curves for spray dried products for 1:1:2 for Ba(NO₃)₂, TiO(NO₃)₂ and C₂H₆N₄O₂ showed a combustion process around 166°C with evolution of heat and loss of weight. There was no further thermal event up to 1000°C. Ba(NO₃)₂ could not complete decompose with less C₂H₆N₄O₂ according to TG/DTA experiments. For C₄H₁₆N₆O₂, the combustion process started around 100°C. In the previous combustion syntheses, the mixed solutions were introduced to a muffle furnace kept at 350°C.
Apparently, $\text{C}_2\text{H}_6\text{N}_4\text{O}_2$ and $\text{C}_4\text{H}_{16}\text{N}_6\text{O}_2$ were good reducing components for the combustion synthesis. These two reagents were prepared by using carcinogenic and expensive hydrazine.\textsuperscript{48} It would be beneficial and pragmatic to use some commercially available and less expensive organic compounds for the combustion synthesis.

Eleven soluble organic compounds were tried as reducing agents by adding a solution of them to the solution having a 1:1 molar ratio of $\text{Ba(NO}_3\text{)}_2$ and $\text{TiO(NO}_3\text{)}_2$ prior to spray drying. Precipitates formed immediately when oxalic acid, citric acid tartaric acid and malic acid were added. Oxalic acid, citric acid and tartaric acid are coprecipitating agents for $\text{Ba}^{2+}$ and $\text{TiO}^{2+}$.\textsuperscript{17} The precipitate formed by adding malic acid contained titanium only, as indicated by the XRD pattern of the calcined powder.

Maleic acid, malonic acid and succinic acid behaved poorly in the combustion process. The TG/DTA curve in Fig. 2.3 for the spray dried product containing maleic acid showed very mild exothermic event around 300-400°C and endothermic melting/decomposition of $\text{Ba(NO}_3\text{)}_2$ around 580°C. Excessive amounts of these organic
Figure 2.3 TG/DTA for 1:1:1 Ba(NO$_3$)$_2$, TiO(NO$_3$)$_2$, Maleic Acid
compounds did not change the characteristic of the TG/DTA curve much and some barium nitrate was always present after the initial reaction. Gluconic acid did produce a violent exothermic reaction around 140°C, however, multiple steps always followed and barium nitrate did not decompose completely. The behavior of glycine was similar to gluconic acid for this purpose.

The best choices were α(±)-alanine and β-alanine (Aldrich, 99+%). Figure 2.4 is the TG/DTA curve of the spray dried product for 1:1:1 molar ratio of Ba(NO$_3$)$_2$, TiO(NO$_3$)$_2$ and α(±)-alanine. This exhibited a highly exothermic event with a major weight loss starting at 200°C. There were no further thermal events up to 1000°C. This is the ideal result for the combustion synthesis. The features of the TG/DTA curve did not change when the molar ratio among Ba(NO$_3$)$_2$, TiO(NO$_3$)$_2$, α(±)-alanine was varied from 1:1:1.5 to 1:1:2. However, an endothermic peak for the melting/decomposition of Ba(NO$_3$)$_2$ appeared around 580°C when the ratio was 1:1:0.8. As a result, the 1:1:1 ratio appears optimum. For β-alanine, the results were very
Figure 2.4 TG/DTA for 1:1:1 Ba(NO₃)₂, TiO(NO₃)₂, α(±)-alanine
similar except that the exothermic event started at 223°C. Powder XRD confirmed that the decomposed powder was BaTiO₃.

For the TG/DTA runs that exhibited a combustion process, almost all reaction products flew out the open sample pan during the tests. A cover of platinum gauze (100 mesh woven from 0.762 mm diameter wire, Johnson Matthey Co., Ward Hill, MA) was used for these runs. It allowed gaseous by-products to escape and kept most of the solid product in the sample pan. Figure 2.4 shows a run with platinum gauze on the sample pan. The amount of sample was adjusted so that the combustion process did not blow the gauze away. However, a small amount of solid product still escaped through the gauze.

Previous studies showed that there existed an ideal ratio between oxidizing and reducing reagents that would release maximum amount of energy for each mole of solid product. Within some range of composition between the oxidizing and reducing agents, the combustion reactions still went completely. The energy released from the reaction was sufficient to decompose any excess amount of oxidizing or reducing reagent. Beyond the range, extra oxidizing or
reducing reagent existed after the combustion reaction and there would be more than one reaction.\textsuperscript{35a,35b} This conclusion also applied for the combustion synthesis for BaTiO\textsubscript{3}. Within the acceptable range, the amount of alanines added to the mixed solution of Ba(NO\textsubscript{3})\textsubscript{2} and TiO(NO\textsubscript{3})\textsubscript{2} did not affect the completion of the combustion process. Since the alanines were just used as reducing agents, the minimum amount would be optimum. On the other hand, the amount of reducing agents, and therefore the temperature the process would reach, might influence the particle size and morphology of the reaction products.

DSC has been used to measure the enthalpy of the combustion for the synthesis of high-T\textsubscript{c} superconductor.\textsuperscript{35a,35b} DSC has also been applied to determine the enthalpy of combustion for graphite, C\textsubscript{60} and C\textsubscript{70}, and the enthalpy of formation of C\textsubscript{60} was estimated based on the measurement.\textsuperscript{49} The attempt to measure the enthalpy for the combustion process for the synthesis of BaTiO\textsubscript{3} did not yield consistent results. The combustion process always raised the sample holder cap and even the heat sink cover of the DSC. Therefore, the DSC baseline was significantly shifted and significant heat escaped detection.
Consequently, the enthalpy for the process was hard to estimate. Similar behavior also had been observed before.\textsuperscript{35} Besides, the estimated enthalpy for the process heavily depended on the amount of sample tested. The accurate DSC measurement relies on adequate heat exchange between sample pan and sample holder.\textsuperscript{50} The combustion synthesis was a very fast reaction, the inadequate DSC results were expected in some sense.

When Ar or $O_2$ was used as a purge gas for these TG/DTA runs, the curves hardly changed from those of air. The combustion processes were indeed internal oxidation-reduction reactions. Not all competitive combustion processes are completely internal. The effect of purge gases has been observed on TG/DTA runs for EDTA-gels, which were prepared from metal nitrate solutions with appropriate amount of EDTA for the synthesis of lead zirconate titanate.\textsuperscript{51} Ambient oxygen participated in that combustion process and the reaction was not totally internal.

The combustion reactions appear to be catalytic reactions. For the combustion synthesis of BaTiO$_3$, there were violent exothermic
reactions in the TG/DTA runs if the mixtures were Ba(NO₃)₂, TiO(NO₃)₂ and alanines, even if the amount of alanine was small. However, there was no violent reaction if aliphatic carboxylic acids (acetic acid, malonic acid etc.) were used as the reducing agent. On the other hand, there always were violent exothermic reactions in the combustion synthesis of high-Tₐ superconductors when either aliphatic carboxylic acids or alanines were used as reducing agents. The reactions were between nitrate and organic components in the presence of specific metal ions. Whether the combustion occurs or not seems related to the existence of particular metal ions. The details of the catalytic nature are beyond this study.

2.6. Preparing Bulk Quantities of BaTiO₃

Figure 2.5 is the flowsheet of the combustion synthesis for BaTiO₃. Approximately 40 grams of BaTiO₃ were prepared according to Fig. 2.5 using either α(±)-alanine and β-alanine as reducing components. The concentration of TiO(NO₃)₂ was about 0.2 M. Similar concentrations of Ba(NO₃)₂ and alanines were prepared by
10 ml TiCl₄ + 50 ml cold H₂O

1 liter 1.5 M NH₃

washed till Cl⁻ free

TiO₂·nH₂O

1.4 M HNO₃

0.2 M TiO(NO₃)₂ (gravimetrically analyzed)

mixed with Ba(NO₃)₂ and alanine in a 1:1:1 molar ratio, spray dried

Spray dried product

heated to 300°C

BaTiO₃

Figure 2.5 Flow Sheet for the Combustion Synthesis of BaTiO₃
dissolving them in distilled water. The three solutions were mixed and spray dried. The spray dried products were hygroscopic and kept dry in a vacuum desiccator. They were then decomposed in a two liter beaker that was placed on a hotplate with its temperature adjusted to 300°C. The powder was added slowly in small quantities and though the reactions were violent, almost all of the product remained in the beaker. The yield of BaTiO₃ based on the amount of starting materials was approximately 60%. The remainder was lost as fine powder in exhaust air of the spray dryer and as a coating on the wall of the spray dryer. A commercial process would have a much higher yield.

2.7. The Spray Dried Products and As-decomposed Powders

Powder X-ray diffraction data were obtained using a Scintag PAD5 powder diffractometer with CuKα radiation at 0.5° (2θ) per minute. The spray dried powder of 1:1:1 molar ratio Ba(NO₃)₂, TiO(NO₃)₂ and α(±)-alanine examined by XRD showed a weak Ba(NO₃)₂ pattern only (see lower curve of Fig. 2.6). This was common among all spray dried products with equal mole of barium salt and
Figure 2.6 Room Temperature XRD results for Spray Dried powder and As-decomposed Product
titanyl nitrate, together with a reducing compound. Even the one started with a solution of Ba(CH₃COO)₂, TiO(NO₃)₂ and additional amount of acetic acid also showed a Ba(NO₃)₂ pattern. It was due to the low solubility of Ba(NO₃)₂ (see section 2.5). Such a phenomenon was also observed in the spray dried products for high-Tc superconductor precursors.³⁵

The XRD result was consistent with the amorphous spray dried powder of TiO(NO₃)₂ solution observed by XRD. The exact form of the titanium salt in the spray dried product was undetermined. The TG/DTA of the spray dried product (vacuum dried) of TiO(NO₃)₂ solution showed a major weight loss around 240°C which was exothermic. Evolved gas analysis by FTIR revealed H₂O and NO₂ in the exhaust. The total weight loss to 1000°C was about 41%. The loss did not fit the assumption that the spray dried product of TiO(NO₃)₂ solution was TiO(NO₃)₂, TiO₂·nH₂O or any simple formula. The intrinsic decomposition process in the absence of any combustion is endothermic, however, the conversion from an amorphous or microcrystalline form to a well crystallized TiO₂ is exothermic.
The alanines in spray dried products were apparently amorphous and in their nitrate forms, as an excess of nitric acid was present. The alanines and titanium compounds in the spray dried products were composed of light chemical elements, would show a weak diffraction pattern if they did partially crystallize. This could be the other reason for the apparent amorphism of these compounds. The same phenomenon was observed for finely divided metal titanium and TiO₂ during the synthesis of BaTiO₃ in a recent study.

When combustion synthesis was used for the preparation of oxide superconductors, the decomposed powder had to be further calcined at 820°C to 910°C for ten minutes to produce the desired phases. This subsequent calcination, however, does not seem required for the formation of BaTiO₃. The upper curve in Fig. 2.6 is the XRD result for as-decomposed powder of the spray dried powder of 1:1:1 molar ratio Ba(NO₃)₂, TiO(NO₃)₂ and α(±)-alanine. All the major peaks are for cubic BaTiO₃. The tiny peak (around 24°, 2θ) is due to small amount of BaCO₃ in the as-prepared BaTiO₃. The detailed characterization of this BaTiO₃ powder will be discussed in coming chapter.
2.8. Combustion Synthesis for BaTi$_4$O$_9$ and Pb$_x$Ba$_{1-x}$Ti$_4$O$_9$

One advantage for the combustion synthesis of BaTiO$_3$ is that it is readily applicable to the synthesis of other compounds in the BaO-TiO$_2$ system. BaTi$_4$O$_9$ is another technically important compound in the system. The only reported low temperature synthesis for the compound is by sol-gel processing.$^{30}$

The combustion synthesis for BaTi$_4$O$_9$ plainly imitated that of BaTiO$_3$. Ba(NO$_3$)$_2$ solution and TiO(NO$_3$)$_2$ solution were mixed in a 1:4 molar ratio basis and $\beta$-alanine was used as reducing component for the combustion synthesis. Mixed solutions of 1:4:1, 1:4:1.5 and 1:4:2 molar ratios of Ba(NO$_3$)$_2$, TiO(NO$_3$)$_2$ and $\beta$-alanine were spray dried. The TG/DTA for the spray dried powder of 1:4:1 showed a major exothermic process with major weight lost around 223°C, and a very small endothermic event corresponding to melting/decomposition of Ba(NO$_3$)$_2$. The TG/DTA for the spray dried products of 1:4:1.5 and 1:4:2 showed the major exothermic process only.

The spray dried products were decomposed in a two liter beaker, as before at 300°C. The as-decomposed powder made from 1:4:1 was
amorphous based on XRD, and it had to be heated to 800°C for ten minutes to convert it to crystalline BaTi$_4$O$_9$. The XRD results for both of the as-decomposed products of 1:4:1.5 and 1:4:2 showed BaTi$_4$O$_9$ pattern. The TG/DTA displayed a difference between these two products. The powder made by 1:4:2 exhibited almost no weight loss up to 1100°C, and the powder made by 1:4:1.5 showed 1.5% weight loss up to 1100°C. So, the 1:4:2 ratio for Ba(NO$_3$)$_2$, TiO(NO$_3$)$_2$ and β-alanine seems optimum for the combustion synthesis. The influence of amount of reducing compound on the enthalpy of combustion reaction and therefore the formation of crystalline product was also observed in a recent synthesis of La$_{0.84}$Sr$_{0.16}$MnO$_3$.$^{53}$

The maximum performance for BaTiO$_3$ based ceramics is achieved through substitution and doping of BaTiO$_3$. The pure BaTi$_4$O$_9$ also does not have an optimum performance, and its properties can also be altered by substitution and doping.$^{4,13,54}$ Therefore, preparation of doped and substituted BaTi$_4$O$_9$ is of great technical interest. Lead was chosen as a major substitution for barium in this study.
The attempt to prepare PbTi$_4$O$_9$, which has never been synthesized, by the combustion synthesis failed. The as-decomposed product for the spray dried powder of 1:4:2 of Pb(NO$_3$)$_2$, TiO(NO$_3$)$_2$ and β-alanine showed a XRD diffraction pattern of PbTi$_3$O$_7$, which was reported stable only up to 850° C. Calcination of the as-decomposed product at 800° C did not change its XRD pattern. It decomposed to PbTiO$_3$ and TiO$_2$ upon heating to 900° C.

Pb$_{0.1}$Ba$_{0.9}$Ti$_4$O$_9$, Pb$_{0.2}$Ba$_{0.8}$Ti$_4$O$_9$ and Pb$_{0.5}$Ba$_{0.5}$Ti$_4$O$_9$, however, were synthesized by spray drying solutions of 1:9:40:20, 1:4:20:10 and 1:1:8:4 molar ratios of Pb(NO$_3$)$_2$, Ba(NO$_3$)$_2$, TiO(NO$_3$)$_2$ and β-alanine. These spray dried products were then decomposed as done for BaTi$_4$O$_9$. Figure 2.7 shows the XRD results, which confirmed that these as-decomposed products were the desired solid solutions. The characterization of BaTi$_4$O$_9$ and Pb$_x$Ba$_{1-x}$Pb$_4$O$_9$ will be discussed in chapter four.
Figure 2.7 XRD Results for BaTi$_4$O$_9$ and Pb$_b$Ba$_{1-x}$Ti$_4$O$_9$. Relative Intensity
2.9. Summary

$\text{BaTiO}_3$, $\text{BaTi}_4\text{O}_9$ and $\text{Pb}_x\text{Ba}_{1-x}\text{Ti}_4\text{O}_9$ (where $x$ is 0.1, 0.2 or 0.5) have been synthesized by a newly developed combustion process. The process started with solutions of appropriately selected reactants. These reactants were intimately mixed by spray drying the solutions. The spray dried products were heated to 300°C to start incandescent reactions, which converted the spray dried products directly to the desired products. Since the reactants were closely mixed throughout the process, this process guarantees homogeneous products that are highly desirable in ceramic processing. High temperature calcination, which is almost indispensable in conventional ceramic processing, is avoided in this process.

One advantage of this method is its applicable to the synthesis of the other compounds in the BaO-TiO$_2$ system. Another advantage of the method should be the relative ease and uniformity with which dopants and major substitutions such as La, Pb, Sr etc. are introduced at the solution stage. It can thus be used to prepare doped and multicomponent BaO-TiO$_2$ based ceramics.
As this processing starts with all reactants in a solution, it can also be utilized to deposit thin films of the products by using an aerosol generator.\textsuperscript{56} Ferroelectric thin films are of great technical interest and have many potential application in microelectronics.
CHAPTER III
Characterization of the BaTiO₃

3.1. TG/DTA/EGA-FTIR for the Thermal Analysis and Residual Carbonate in As-decomposed Powder

Figure 2.6 shows that the as-prepared BaTiO₃ still contained a small amount of BaCO₃. Thermal analysis of the powder was carried out by simultaneous thermogravimetry, differential thermal analysis and evolved gas analysis (TG/DTA/EGA). A Seiko TG/DTA 320 was used for TG/DTA and a Bio-Rad FTS-40 Fourier Transform Infrared (FTIR) spectrometer was used for EGA. The exhaust of the TG/DTA was passed to a sample cell of the FTIR. The temperature of the sample cell and the gas line of the exhaust was kept above 200°C. Figures 3.1 and 3.2 show the results of the thermal analyses. There was no evident endothermic or exothermic process based on the DTA. The type R thermocouple used for DTA was not sensitive enough to detect
Figure 3.1 TG/DTA Weight Loss of the As-prepared Powder vs Temperature
Figure 3.2 Evolved Gas Analysis Corresponding to Fig. 3.1.

Total FTIR Absorption vs Time (upper). FTIR Spectrum at 30.41 minute, corresponding to ~ 800°C at Fig. 3.1 (lower).
small changes in enthalpy. The total weight loss up to 1200°C was about 2%. There was a slow weight loss of about 1% up to 700°C. The other 1% between 700 to 820°C was due to conversion of BaCO₃ to BaTiO₃ by reacting with TiO₂. The EGA did not detect any gas for the early weight loss, which was presumably due to the low sensitivity of IR to some gases. A clear peak in the EGA for CO₂ was observed during the weight loss corresponding to the conversion of BaCO₃ to BaTiO₃.

The formation of BaCO₃ during the chemical processing of BaTiO₃ has been widely observed in coprecipitation, hydrothermal and sol-gel processing. It was also observed in the preparation of Y-Ba-Cu-O base high-Tₚ superconductors. BaCO₃ is a very stable carbonate and is also very easy to form, even CO₂ in air is sufficient for the formation of BaCO₃. A lot of CO₂ was produced in the combustion synthesis of BaTiO₃, so the formation of some BaCO₃ was anticipated. The formation of BaCO₃ "islands" in the sol-gel processing ruined that as a homogeneous technique for BaTiO₃ processing.
The decomposition of BaCO$_3$ depends on the chemical environment and CO$_2$ pressure. BaCO$_3$ by itself can be stable in air to a high temperature. BaCO$_3$ mixed with TiO$_2$ (anatase) starts to decomposed around 700°C by the formation of BaTiO$_3$ at the boundary between the components.\textsuperscript{9} There is a difference between BaCO$_3$ "islands" formed in wet chemical processing and BaCO$_3$ as a reactant in a solid-state reaction. BaCO$_3$ and TiO$_2$ are well mixed during chemical processing and therefore complete conversion to BaTiO$_3$ usually happens below 900°C.\textsuperscript{29,58,59}

By heating the as-prepared BaTiO$_3$ at 800°C for thirty minutes, the small peak of BaCO$_3$ in Fig. 2.6 disappeared. However, the TG/DTA still indicated some weight loss corresponding to the conversion of BaCO$_3$ to BaTiO$_3$. XRD is not very sensitive to the detection of a small amount of second phase.\textsuperscript{52} The TG in Fig. 3.1 shows complete weight loss for BaCO$_3$ by 820°C. As the conditions for purging CO$_2$ from relatively large quantities in a regular furnace were not as good as those for milligram quantities in a TG/DTA
furnace, carbonate in as-prepared BaTiO$_3$ could not be entirely eliminated until the powder was calcined at 900°C for an hour.

3.2. Stoichiometric Analysis by X-ray Fluorescence Spectrometry

It is well known that the stoichiometry has important influences on the sinterability of the powder as well as the dielectric and mechanical properties of the ceramic. For the combustion synthesis of BaTiO$_3$, the barium to titanium ratio was carefully controlled at 1.00. TiO(NO$_3$)$_2$ solution was weighed to determine the moles of titanium. Then solid Ba(NO$_3$)$_2$ was weighed to match the moles of titanium. Therefore, the moles between the two components in the product should be equal.

The molar ratio of the as-prepared BaTiO$_3$ was measured by X-ray fluorescence spectrometry using a Seiko SEA 2001 X-ray fluorescence spectrometer. It was done in our research group, by Todd T. Magee as part of his Master's thesis.$^{60}$ The BaTiO$_3$ sample was dissolved in sodium tetraborate flux. A fused glassy disk, which was homogeneous, would develop upon cooling the flux. The
concentrations of BaO and TiO$_2$ in the fused sodium tetraborate were determined by XRF spectroscopy independently, using external standard calibration curves. The ratio of BaO to TiO$_2$ in the as-prepared BaTiO$_3$ was found $1.003\pm0.006$.

3.3 The Evolution of Room Temperature XRD, XRD Line Broadening and Crystallite Size with Calcination Temperature and Time

Besides stoichiometry and purity, particle size is also an important indicator of the quality of BaTiO$_3$ powder. Fine powder BaTiO$_3$ is, in general, preferred in processing as it tends to sinter more readily and can yield a finer grain size.$^{3,15}$ Pure BaTiO$_3$ exhibits its highest dielectric constant with about 1 $\mu$m grain size and very high density.$^{16}$ Consequently, to synthesize high purity, homogeneous and submicron powders of BaTiO$_3$ is the general goal of wet chemical methods.$^{17}$ Combustion methods generally yield a fine particle product, since extensive gaseous by-products produced during the process inhibited particle growth.$^{19,35-39}$ The XRD pattern of the as-prepared BaTiO$_3$ was cubic, indicative of finely divided BaTiO$_3$.$^{1,17,61}$
For fine powder BaTiO₃, the cubic structure at room temperature is widely observed. This is the subject of many speculations. In every case, the cubic structure will convert to the tetragonal structure after the powder is calcined at high temperature. The fine powder always becomes coarse upon calcination. This phenomenon was first noticed for the submicron BaTiO₃ prepared by the "oxalate process" using a low temperature decomposition with nitrogen purge gas, for powders prepared by the hydrolysis of titanium isopropoxide in barium hydroxide solution, and for powders synthesized by the simultaneous hydrolysis of hydrolysis of alkoxides of barium and titanium in an alcoholic solution. As all the cubic BaTiO₃ was prepared at relative low temperature, an early argument was that the powder still absorbed some moisture, organic solvent or carbon dioxide and therefore had a defect structure. It was believe to be metastable, which was in accordance with the observation that cubic would change to tetragonal upon calcination.

With the increase in accuracy of the measurement, it was found that absorbent free BaTiO₃ also assumed cubic structure if it was very
fine. Such behavior was similar to that of ZrO$_2$ where fine powder took a different crystal structure from coarse powder.\textsuperscript{64} One fact is that the enthalpy of these phase transitions are rather small. Therefore, another theory assumes that different crystal structures have different surface energy and this is the cause. With decreasing particle size, the surface energy has increasing importance in the overall Gibbs free energy. At some critical size, the difference of surface energy overcomes the small enthalpy difference, which makes BaTiO$_3$ cubic at room temperature.\textsuperscript{61,64} The cubic BaTiO$_3$ at room temperature is not metastable according to this theory. A recent thermodynamic analysis predicts that the minimization of total Gibbs free energy among the internal strain, ferroelectric domain wall energy etc. is the cause of this unique incident.\textsuperscript{16,62}

Cubic BaTiO$_3$ at room temperature is also observed in thin films. Films within a certain thickness are always cubic at room temperature.\textsuperscript{3} Processing conditions do not affect the crystal structure.

The XRD pattern not only determines the crystal structure, it also can be used to measure crystallite size, which is equivalent to the
smallest size measured by transmission electron microscope (TEM).\textsuperscript{52}
The equivalence has been confirmed by many observations.\textsuperscript{19,52,65} As sintering happens rapidly for this BaTiO\textsubscript{3} powder above 1100°C (see section 3.6), the BaTiO\textsubscript{3} was calcined at various temperature below 1100°C and for different time at 1100°C prior to XRD examination. Figure 3.3 is the XRD patterns at room temperature for BaTiO\textsubscript{3} powder as a function of calcination temperature and time. Conversion of the cubic phase to the tetragonal phase, as evidenced by the splitting of the 200 peak around 45° (2θ) and growth of particle size, is not complete until the powder had been calcined at 1100°C for five hours.

Figure 3.3 shows a gradual splitting and narrowing of XRD peaks as heat treatment is increased. The XRD line broadening reflects crystallize size in a solid that is always smaller than its physical size that can be observed under microscope.\textsuperscript{52} The crystallite size is determined by the breadth at half peak based on the Scherrer formula,\textsuperscript{52}

\[ t = \frac{0.9\lambda}{B \cos \theta} \]  \hspace{1cm} (2)

where \( t \) is the mean dimension of the crystallites composing the
Figure 3.3 XRD results at Room Temperature for BaTiO$_3$ as a Function of Calcining Temperature and Time
powder, \( \lambda \) is the wavelength of the X-ray that is equal to 0.15406 nm in this case, \( \theta \) is the angle of diffraction, and \( B \) is the breadth at half peak of the diffraction profile on the 2\( \theta \) scale in radians. The mean crystallite sizes of the BaTiO\(_3\) calculated based on the Scherrer formula are listed in Table 3.1. The crystallite size increased from 0.034 \( \mu \text{m} \) for the as-prepared powder to 0.072 \( \mu \text{m} \) after calcination at 1100\( ^\circ \text{C} \) for five hours.

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>( B ) (radian)</th>
<th>( t ) (( \mu \text{m} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-prepared</td>
<td>0.00428</td>
<td>0.0337</td>
</tr>
<tr>
<td>½ hour @ 800( ^\circ \text{C} )</td>
<td>0.00367</td>
<td>0.0393</td>
</tr>
<tr>
<td>1 hour @ 900( ^\circ \text{C} )</td>
<td>0.00332</td>
<td>0.0434</td>
</tr>
<tr>
<td>1 hour @ 1000( ^\circ \text{C} )</td>
<td>0.00314</td>
<td>0.0459</td>
</tr>
<tr>
<td>1 hour @ 1100( ^\circ \text{C} )</td>
<td>0.00305</td>
<td>0.0472</td>
</tr>
<tr>
<td>2 hour @ 1100( ^\circ \text{C} )</td>
<td>0.00279</td>
<td>0.0516</td>
</tr>
<tr>
<td>5 hour @ 1100( ^\circ \text{C} )</td>
<td>0.00201</td>
<td>0.0717</td>
</tr>
</tbody>
</table>

Table 3.1 Average Crystallite Size of BaTiO\(_3\) Powder as a Function of Calcining Temperature and Time
3.4. DSC Measurements for the BaTiO₃ with Different Heat Treatments

There is not a clear distinction between the cubic and the tetragonal BaTiO₃ as Fig. 3.3 showed. Besides XRD measurements, DSC is frequently used to determine the Curie temperature and the enthalpy of the tetragonal to the cubic phase transition. The change in enthalpy or heat capacity is measured as the temperature is scanned. The degree of tetragonality has been defined as proportional to the enthalpy of the phase transition.²⁶ᵃ On the other hand, BaTiO₃ powder samples with different size fractions prepared by grinding a pellet that was sintered at 1350°C for three hours and presumable completely tetragonal, showed a varying enthalpy for the phase transition and a slight difference in Curie temperature.⁶² The enthalpy of the phase transition for the size between 38-43 μm was about two thirds of that for the size between 74-104 μm. The difference was attributed to the variation in internal strain due to different powder size.⁶²

The DSC measurement was performed using the TA Instruments, Inc. DSC 2920 module of a 2100 system. Indium and tin were used for temperature and enthalpy calibration. BaTiO₃ powder was put in an
open Al sample pan. The heating rate was 2°C/min and nitrogen at 25 ml/min was used as purge gas. For as-prepared powder and powder calcined at 800°C, there was not a detectable phase transition. Commercial high purity BaTiO₃ (TAM Ceramics Inc., Niagara Falls, NY) made by the "oxalate process" did not show the phase transition either. The Curie temperature was determined based on the onset temperature of the event. The apparent enthalpies of the phase transition and the Curie temperatures was listed in Table 3.2. There is an increase in both the Curie temperature and the apparent enthalpy of the phase transition with increasing particle size.

Table 3.2 The Curie Temperature and the Apparent Enthalpy of the Cubic to the Tetragonal Phase Transition with Various Heat Treatment

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Curie Temp (°C)</th>
<th>ΔH (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hour @ 900°C</td>
<td>119.7</td>
<td>0.18</td>
</tr>
<tr>
<td>1 hour @ 1000°C</td>
<td>120.4</td>
<td>0.28</td>
</tr>
<tr>
<td>1 hour @ 1100°C</td>
<td>120.8</td>
<td>0.49</td>
</tr>
<tr>
<td>2 hours @ 1100°C</td>
<td>124.7</td>
<td>0.71</td>
</tr>
<tr>
<td>5 hours @ 1100°C</td>
<td>128.5</td>
<td>0.72</td>
</tr>
</tbody>
</table>
The variations in the Curie temperature and enthalpy due to different particle size have been reported before.\textsuperscript{26a,62,66,67} The increasing enthalpy of the phase transition with the particle size has been observed frequently, although some investigators found little or no change in the Curie temperature with different particle size.\textsuperscript{26a,59} Others noticed a considerable drop in the Curie temperature with decreasing particle size.\textsuperscript{63,64} Particle size and thermal treatment were only part of the factors that decided the structure of the material. Other factors during the processing of the material might also affect the properties of the material.

The most frequently used methods to determine the cubic (paraelectric) or the tetragonal (ferroelectric) phase of BaTiO\textsubscript{3} are XRD, DSC, and impedance measurement (see Section 3.9). For fine powder, extensive line broadening makes XRD unsuitable to distinguish the two phases. Figure 3.3 clearly shows such a difficulty. DSC and impedance measurements also give the same indecisive situation. Raman spectroscopy has been used recently to investigate the phases of BaTiO\textsubscript{3}.\textsuperscript{26b,26c} This method can detect if the titanium ions
are off the center of the octahedra. It was surprising to find that the ultrafine BaTiO$_3$ made by hydrothermal method showed same Raman spectrum as coarse powder. Therefore, the titanium ions were off the center of the octahedra in the so-called cubic BaTiO$_3$. When the temperature of the ultrafine powder was raised above 140°C, Raman spectrum showed the titanium ions were in the center. Raman spectroscopy clearly detected the phase transition, which XRD and DSC cannot.

3.5. Individual and Agglomerate Size of the BaTiO$_3$

Particle size usually means individual particle size or physical size, which can be observed by microscope or can be determined by surface area measurement (BET technique). Individual particle size is similar to grain size in sintered ceramics. The formation of grain and grain bonding starts from individual particle. Submicron powder indicates the individual particle size is below a micron. Therefore, the measurement of individual particle size is also an important part for powder characterization.
Scanning Electron Microscopy (SEM)\textsuperscript{68} is a powerful technique to observe the surface structure of a solid sample. SEM has much higher magnification than conventional optical microscopy. It is widely used to observe microstructure of biological, mineral and other samples. A commercial scanning electron microscope usually reaches a resolution of 5 nm. SEM can be used to observe conducting samples directly. A nonconducting sample must be coated with a layer of carbon or gold before the observation. Higher resolution can be obtained from gold coating, but this will also affect any quantitative chemical element microanalysis.\textsuperscript{68}

A JOEL JSM-820 Scanning electron microscope, operating at 15 KV accelerating voltage, was used to observe the particle size and morphology. The samples were prepared by sprinkling some powder onto aluminum stubs that were covered with a double sided tape. A gold layer was then coated on the samples by sputtering. The as-prepared powder displayed a very rough surface that was presumably caused by rapidly evolved gaseous by-products during the processing. The particle size was about 0.1 \(\mu\)m. This was consistent with
equivalent particle size based on physical absorption of a monolayer of nitrogen (BET technique). Little particle growth was observed by heating the powder at 800°C and 900°C, but increased quickly when the temperature was above 1000°C. The particle size was close to 1 \( \mu \text{m} \) after the powder was calcined at 1100°C for two hours. The (a) part of Fig. 3.4 is a scanning electron micrograph that revealed the agglomerates consisted of millions of submicron particles for the powder that was calcined at 900°C for an hour. The (b) part showed that the particle size grew significantly upon heating at 1100°C for two hours.

Particle specific surface area was determined using a Micromeritics Pulse Chemisorb 2700 by single-point BET adsorption method. The as-prepared sample was degassed at 300°C for 30 minutes before the measurement. Both adsorption and desorption measurements were made using nitrogen as the detector gas and helium as the carrier gas. The measured specific surface area was 8.2 m\(^2\)/g. An equivalent particle size was calculated with an assumption that all
Figure 3.4 Scanning Electron Micrograph Showing the Morphology of BaTiO₃ Agglomerates Prepared by Fig. 2.5.

(a) is after Calcining at 900°C for One Hour (lower).

(b) is after Calcining at 1100°C for Two Hour (upper).
particles were identical spheres. The formula for the calculation is

\[ d = \frac{6}{\rho s} \]  

(3)

where \( d \) is the diameter of the sphere, \( \rho \) is the density, and \( s \) is the specific surface area, which gave an equivalent spherical diameter of 0.12 \( \mu m \). It was obvious that the particles observed under microscope were not single crystal. They were composed of crystallites having an average size of 0.034 \( \mu m \). The gaps between the crystallites are so small that nitrogen molecule can hardly penetrate. Similar phenomena were also observed in another combustion synthesis.\(^{19}\) Powders made by hydrothermal, coprecipitation and solid-state methods have a much closer correspondence between the crystallite size and the individual particle size.\(^{66}\)

The size of agglomerates was measure by Fraunhofer laser diffraction.\(^{69}\) A Coulter CS130 was used for measuring the agglomerate size of as-prepared \( \text{BaTiO}_3 \). The instrument is capable of measuring agglomerate sizes and distribution in the range of 0.1-900 \( \mu m \). About 2 grams of powder were suspended in 2-propanol for the
Figure 3.5 Distribution of Agglomerate of As-prepared \( \text{BaTiO}_3 \), Measured by Fraunhofer Laser Diffraction
measurement. The measurement took 95 seconds and numerous diffraction data were taken. The particle sizes were determined based on the angle of diffraction. Figure 3.5 is the result of the measurement, which had a Gaussian-type distribution. The mean size was 69.56 $\mu$m and the median size was 41.95 $\mu$m. The results were very similar when the powder was suspended in water.

Crystallite size, individual size and agglomerate size are three different levels of powder size. The material on the surface has different properties from the bulk part. Surface energy, and therefore particle size, affects various properties of powder. It has an especially important influence on sintering.

3.6 Sintering and Thermodilatometry

After a ceramic powder is prepared, it must be pressed and fired to become a strong, durable product for practical functions. The firing process is also known as sintering. The process is quite simple to operate, although the mechanisms that determine the final microstructure and properties are very complicated. Sintering is the
bonding together of particles when heated to high temperature. This is the result of atomic diffusion. The usual sintering temperature is a few hundred °C below the melting temperature of the corresponding ceramic powder. The thermodynamic force behind the process is the reduction of surface area and therefore surface energy. As a result, a fine powder having a high surface area is more active in the process. This is the same reason that fine powder will become coarse upon calcination. During sintering, fine powders either fuse together to form large grains or build bonding between closely packed particles by eliminating pores. These two procedures happen simultaneously and one is dominant dependent on temperature and other sintering conditions.

Sintering is similar to ordinary chemical reactions, in that it is a time-dependent and temperature-dependent processes. TG, DTA and thermodilatometry (TD) that can determine weight, heat, and shrinkage during sintering are common macroscopic means to study the process. Usually, sintering additives are added and mixed with powder before pressing. Sintering additives that change packing of powders in
pressed pellets have two major functions. They can improve the mechanical properties of unfired (green) bodies, which make pressed pellets less brittle and easy to handle. They can also modify the sintering process, e.g., liquid phase formation, and yield a better sintered product. One common additive for the first purpose is polyvinyl alcohol.

The $\text{BaTiO}_3$ was pressed without additives to simplify the sintering process. Attempts to sinter pressed pellets of as-prepared $\text{BaTiO}_3$ always resulted in the formation of blisters on the surface, which were presumably caused by the residual carbonate. Hence, $\text{BaTiO}_3$ calcined at 900°C for an hour was used for the subsequent sintering study. There was not any significant results from a TG/DTA run as anticipated. The energy released due to reducing surface area was too small to be detected by DTA.

Green pellets were made by pressing exactly 0.4000 gram of powder in a die, 6.0 mm in diameter, under an applied load of $8 \times 10^3$ Kg/cm$^2$ for 4 minutes. The thickness of the pellets was 3.778 mm. The calculated green density (see section 3.8) was 3.745 g/cm$^3$. 
corresponding to 62% of theoretical density. Maximum packing of uniform spheres is 74% of theoretical density. The sintering was carried out from room temperature to 1400°C using the Seiko Thermal Mechanical Analyzer (TMA) 320 module of a SSC/5200 system for TD measurement. The load was five grams and platinum gauze was put on both sides of the pellets to avoid bonding them to the TMA sample holder or probe. Temperature above 1400°C was avoided to prevent the cubic to hexagonal phase transition at 1460°C that might cause the pellet to crack. As sintering did not start until 750°C, temperature was quickly raised to 500°C. Then five different heating rates of 1°C/min, 2°C/min, 4°C/min, 8°C/min and 16°C/min were used to study the kinetics of the sintering process. Figure 3.6 shows the sintering results, which clearly exhibits three stages of sintering. For all heating rates, the total shrinkage was 14.1%. At the highest heating rate, sintering was complete by 1365°C. Heating to 1400°C was more than adequate for the sintering.
Figure 3.6 Thermодilatometry (lower) and Derivative of Thermodilatometry (upper) of Pressed BaTiO₃ Pellets at Heating Rates of 1°C/min, 4°C/min and 16°C/min
Green pellets were also heated at 4°/min to 1230°C, 1250°C, 1280°C, 1305°C and 1315°C using the same furnace, and then held for four hours to study their dielectric and microstructural properties.

3.7. The Ozawa Method and Activation Energy of Sintering

Sinterability is an important aspect of the powder properties. For the same powder, the sinterability depends on the temperature of sintering, green density, external pressure and sintering additives. Figure 3.7 is the sintering results at 4°C/min for green pellets with densities at and about 1% above and below 3.745 g/cm³. These show that the sintering mechanism did not change in this region of density. The kinetics of sintering was investigated further by TD.

It is very difficult to determine a sintering mechanism and it cannot be resolved by TD alone.15,70 Usually, pellets were heated to a certain temperature for some time and then quenched. The pore sizes were measured by Hg-penetration and the fracture surfaces were examined by SEM to complement macroscopic observations.15,70 Microscopic investigation was not carried out here. Figure 3.6
Figure 3.7 Thermodilatometry (lower) and Derivative of Thermodilatometry (upper) of Pressed BaTiO₃ Pellets with Different Green Density at Heating Rates of 4°C/min
previously showed that three stages of sintering actually overlapped in this range of temperature. The stage of sintering below 1000°C was cause by the ultrafine particles. The pellet made by powder calcined at 1000°C for an hour did not show such a stage of sintering which confirmed that point. The pellet made by commercial high purity BaTiO₃ (TAM Ceramics Inc., Niagara Falls, NY) did not show this stage either.

If the rate of a process obeys the ordinary kinetic equation,

$$\frac{dx}{dt} = A \exp \left( -\frac{E}{RT} \right) f(x)$$  \hspace{0.5cm} (4)

where the left side is the rate and A, E, R, T are pre-exponential factor, activation energy, gas constant, and absolute temperature, respectively. f(x) is a certain function of x that depends on the mechanism of the process. If the process was carried out under constant heating rate and mechanism does or does not change during the heating, the activation energy can be estimated by the Ozawa method. To a certain conversion of the process (some fixed number of x), the Ozawa method predicts,
where \( H \) is the heating rate, \( T_0 \) is the temperature when the process reached the conversion. \( E \) and \( R \) are same as those in the previous equation. The activation energy \( E \) can be determined by carrying out the same process under several different heating rates. The method was initially used for thermal degradation of polymers. It has been recently applied to determine the activation energy of thermal dehydration processes. All these earlier studies were based on TG results.

By taking \( x \) for shrinkage, the Ozawa method was then applied to calculate the activation energy of sintering. Figure 3.8 shows such an approach. For lower conversions of sintering (less than 70% of the total shrinkage), the \( \log H \) vs \( 1/T \) plot did not yield a straight line. As a result, the method did not produce a clear result as the different stages were mixed. At 90% of sintering corresponding to the last stage, the activation energy was estimated to be \( 4.2 \times 10^6 \) J/mole. There is no previously reported value for BaTiO₃. In diffusion controlled sintering,
Figure 3.8 The Ozawa Plot for Sintering

at 10, 30, 50, 70 and 90% of Conversion
the activation energy is believed equal to a substantial fraction of the bond energy. Bond energy and enthalpy of formation for BaTiO$_3$ are not available. The bond energy of BaTiO$_3$ should be slightly higher than the summation of the bond energy of BaO and TiO$_2$. The summation is $1.52 \times 10^7$ J/mole. Since such a process only happens at $1300^\circ$C or above, the very high activation energy is reasonable.

3.8. Density and Grain Size of Sintered BaTiO$_3$ Pellets

The measurement of the density for ceramic product is a routine procedure. The density is not only an important physical properties, it also affects mechanical properties and performance of ceramics. Low density is caused by pores in the ceramic, which are usually detrimental to the performance of the material. The measured density is often expressed as percentage of theoretical density, which is calculated based on crystal structure to be 6.017 g/cm$^3$ for BaTiO$_3$. In polycrystalline ceramic materials, full theoretical density is rarely observed as there are always some pores among the boundaries of the crystallites.
The measurement of density includes the measurements of weight and volume. The weight can be readily determined by a balance. Two frequently used approaches for volume measurement are the geometric method and the Archimedes' method. If the object has a simple geometric shape such as a perfect rectangle or cylinder, its volume can be easily calculated based on its dimensional measurements. Sintered ceramics usually have rough and irregular surfaces, which make geometric measurement less accurate. The Archimedes' method determines the volume of a solid using the buoyancy of the object in some fluid. It is based on the Archimedes' principle: an object placed in a fluid suffers a loss in weight equal to the weight of the fluid which the object displaces. One common fluid for the measurement is water. This measurement of volume excludes any open porosity that is penetrated by the fluid, in contrast to the geometrical measurement.

The density of pellets heated to 1400°C have been measured. There were noticeable dents in the surface and edge of the sintered pellets. Therefore, the density measured by the geometric method was
anticipated to be lower than that by the Archimedes' method. For the geometric method, the diameter and the thickness of the sintered pellet were measured by a micrometer. The calculated density was 5.44 g/cm$^3$, corresponding to 90.4% of theoretical density.

For the Archimedes' method, the weight of the sintered pellet before and during immersion in water was measured with a commercial balance. Based on the weights of the pellet in air and water and the density of water, the density of the pellet can be calculated by the following equation,

$$\rho = \frac{\rho_{\text{water}} W_{\text{air}}}{W_{\text{air}} - W_{\text{water}}}$$  \hspace{1cm} (6)

where $\rho_{\text{water}}$, $W_{\text{air}}$, $W_{\text{water}}$ are the density of water, the weight of the pellet in air and water respectively. The density was 5.63 g/cm$^3$, corresponding to 93.5% of theoretical density. The densities of sintered pellets made by BaTiO$_3$ powder prepared by sol-gel, combustion method and hydrothermal method were reported 90.0%, 92.0% and 96.5% of theoretical density respectively.$^{19,26a,27}$ No sintering additives were used in those studies either. The results here
Figure 3.9 Scanning Electron Micrograph of As-fired Surface of BaTiO₃ Pellet at a Heating Rate of 2°C/min to 1400°C
were comparable to those investigations. Pellets with higher density can be obtained using sintering additives or hot pressing.\textsuperscript{16,27,40}

The grain size of a sintered pellet was determined by SEM. Fractured and as-fired surfaces were examined. The same instrumental and experimental conditions as for powder particle measurement were used. The samples were prepared by cementing the pellets to aluminum stubs. A gold layer was then coated on the samples by sputtering. Figure 3.9 is a typical scanning electron micrograph of the grain structure for as-fired surface. It shows that the grain size in the pellets are between 30 to 40 $\mu$m. The heating rates did not have a discernible effect on grain size.

3.9. Impedance Spectra of the BaTiO$_3$ Pellets

Impedance analysis determines the performance of a ferroelectric compound as a dielectric material for an electronic capacitor. It is an overall evaluation of the material processing.\textsuperscript{3,5} Both the powder preparation and sintering have a significant influence on these results. A computer interfaced HP 4192A impedance analyzer was used for the
measurement of the dielectric properties. The top and bottom surfaces of the sintered pellets were ground and coated with a silver paste. The diameter and thickness of the samples were measured with a micrometer before coating. These samples were then put between two thin silver plates that were connected to the impedance analyzer by silver wires. The samples were heated to 250°C and then allowed to cool at 1°C/min to room temperature during the dielectric measurement at a frequency of 1 kHz. The sample temperature was controlled by an Orton Model 29 controller. At room temperature, the dielectric constants were measured at frequencies from 5.0 to $1.3 \times 10^7$ Hz. Figure 3.10 is the dielectric temperature curve at a frequency 1 kHz. And Fig. 3.11 is the dielectric frequency curve at room temperature. The impedance spectra for the pellets sintered at 1230°C, 1250°C, 1280°C, 1305°C and 1315°C for four hours were also measured.

Figure 3.10 shows a typical curve of the dielectric constant as a function of temperature for BaTiO$_3$. It shows a maximum dielectric constant around the Curie temperature. Over a narrow frequency range, BaTiO$_3$ does not show a strong dependance on frequency. The
Figure 3.10 Dielectric Constant of BaTiO$_3$ as a Function of Temperature at 1 kHz
Figure 3.11 Dielectric Constant of BaTiO$_3$ as a Function of Frequency at Room Temperature
room temperature dielectric constants for all pellets heated at the
different heating rates to 1400°C were very close to 1500. Different
heating rates generated pellets having almost the same dielectric
constant, which was presumed to be due to the similar density and grain
size.\textsuperscript{16} It is well known that the dielectric constant for pure BaTiO\textsubscript{3}
depends on its density and grain size. BaTiO\textsubscript{3} with 99.9\% of
theoretical density and about 1 \( \mu \text{m} \) grain size, prepared by hot pressing,
shows the highest dielectric constant of 5000-6000.\textsuperscript{16} Sintering
conditions, theoretical densities, grain sizes and dielectric constants are
listed in Table 3.3.

The apparent optimal sintering temperature was around 1300°C.
At lower sintering temperature, the porosity was high enough to
undermine the performance of the material. At higher sintering
temperature, grain growth overwhelms the benefit of increased density.
According to Fig. 3.6, 1300°C was the starting temperature of the last
stage of sintering. Table 3.3 shows that the sintered density was
moderately low below that temperature. The observation of grain sizes
with sintering condition listed in Table 3.3 is consistent with a previous investigation.\textsuperscript{67}

Table 3.3. Sintering Conditions, Density, Grain Size and Dielectric Constant of BaTiO\textsubscript{3}

<table>
<thead>
<tr>
<th>Sintering Conditions</th>
<th>Density (% of Theoretical)</th>
<th>Grain Size (μm)</th>
<th>Dielectric Constant (×10\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>to 1400°C</td>
<td>93.5</td>
<td>30-40</td>
<td>1.49</td>
</tr>
<tr>
<td>4hrs@1230°C</td>
<td>82.7</td>
<td>0.5-1</td>
<td>2.24</td>
</tr>
<tr>
<td>4hrs@1250°C</td>
<td>87.8</td>
<td>0.8-2</td>
<td>2.35</td>
</tr>
<tr>
<td>4hrs@1280°C</td>
<td>90.0</td>
<td>1-4</td>
<td>2.57</td>
</tr>
<tr>
<td>4hrs@1305°C</td>
<td>92.8</td>
<td>5-10</td>
<td>2.68</td>
</tr>
<tr>
<td>4hrs@1315°C</td>
<td>94.6</td>
<td>10-20</td>
<td>2.47</td>
</tr>
</tbody>
</table>

The decrease in dielectric constant with decreasing density (increasing porosity) has been observed in many materials.\textsuperscript{5} Both theoretical analysis and experimental results predict that the square root of the dielectric constant for a ferroelectric ceramic is inversely proportional to porosity.\textsuperscript{78} The dependance of the dielectric constant on grain size has been investigated.\textsuperscript{16,79} The results are for small grain size
are partly related to the fact that fine particle BaTiO₃ assumes a cubic structure at room temperature. For grain size less than 1 μm, BaTiO₃ gradually becomes cubic which has a lower dielectric constant than the tetragonal form. For grain size larger than 1 μm, the ferroelectric domain size increases with grain size. Small domain size is attributed to high dielectric constant. This has been observed and predicted by a thermodynamic analysis. The dielectric grain size curve has been measured and analyzed by theoretical models.

3.10. Summary

BaTiO₃ prepared by the combustion method has been characterized. There is a small amount of carbonate in the as-prepared powder, which can be removed by calcination of the powder at 900°C for an hour. Such calcination does not change the fine size of the powder significantly. The particle size has been studied by XRD line broadening, SEM, and Fraunhofer laser diffraction. These reveal the crystallite, individual and agglomerate size respectively. The average
sizes are 0.034, 0.1 and 69.56 μm, which indicates the structure of the powder at three different levels.

Elemental analysis demonstrates a good stoichiometry in the powder. The powder has been pressed and sintered, three stages of sintering are observed by a thermodilatometry. The first stage below 1000°C is due to the fine particle size. The activation energy of the last stage of sintering above 1250°C has been determined by the Ozawa method to be 4.2×10^6 J/mole. Densities, grain sizes and dielectric constants of the sintered pellets have been measured. The pellets sintered by a constant heating rate to 1400°C displayed a 93.5% of theoretical density, 30-40 μm grain size and a dielectric constant at room temperature of 1500. The best dielectric constant observed in this study is 2680. The pellet was sintered at 1305°C for four hours, density and grain size of the pellet were 92.8% and 5-10 μm respectively.
CHAPTER IV

Properties of the BaTi$_4$O$_9$ and Pb$_x$Ba$_{1-x}$Ti$_4$O$_9$

4.1. XRD and SEM of the BaTi$_4$O$_9$ and Pb$_x$Ba$_{1-x}$Ti$_4$O$_9$

BaTi$_4$O$_9$ prepared by the same method did not contain BaCO$_3$, contrary to BaTiO$_3$ prepared by the combustion synthesis. Fig. 2.7 does not show any BaCO$_3$ peak in the XRD pattern and TG/DTA did not exhibit weight loss either. This was similar to the sol-gel synthesis of BaTi$_4$O$_9$, the compound developed directly from amorphous gel without the formation of BaCO$_3$ or other phases.\cite{30} This is presumable due to the excess of TiO$_2$ for the complete reaction of all BaO. On the other hand, the preparation by simultaneous hydrolysis of alkoxides always demonstrated the formation of intermediates and high temperature calcination was indispensable for the phase formation.\cite{127} Pb$_x$Ba$_{1-x}$Ti$_4$O$_9$ materials prepared by the combustion method did not show weight loss in their TG/DTA runs either.
The XRD of the BaTi$_4$O$_9$ did not change with further calcination of the as-prepared powder at 800°C and 950°C. The as-decomposed powder of the spray dried product of 1:4:1 Ba(NO$_3$)$_2$, TiO(NO$_3$)$_2$ and β-alanine must be calcined at 800°C for the formation of the BaTi$_4$O$_9$ phase. In sol-gel synthesis, the BaTi$_4$O$_9$ phase gradually developed between 550°C to 900°C and the weight loss of the gel was not complete until 800°C. This was consistent with the synthesis by spray drying of 1:4:1 of Ba(NO$_3$)$_2$, TiO(NO$_3$)$_2$ and β-alanine. There was a considerable advantage by using 1:4:2 of Ba(NO$_3$)$_2$, TiO(NO$_3$)$_2$ and β-alanine, pure BaTi$_4$O$_9$ can be obtained without further calcination.

The BaTi$_4$O$_9$ and Pb$_x$Ba$_{1-x}$Ti$_4$O$_9$ powders have been inspected by SEM using the same instrument, operational conditions and sample preparation as for BaTiO$_3$ in the previous chapter. Particle size and structure are very similar among BaTi$_4$O$_9$, Pb$_{0.1}$Ba$_{0.9}$Ti$_4$O$_9$, Pb$_{0.2}$Ba$_{0.8}$Ti$_4$O$_9$ and Pb$_{0.5}$Ba$_{0.5}$Ti$_4$O$_9$. Figure 4.1 is the micrographs of the BaTi$_4$O$_9$, which shows a spherical particle around 1 μm. A close examination revealed holes and cracks on the particles. The spherical
Figure 4.1 Scanning Electron Micrograph of as-prepared $\text{BaTi}_4\text{O}_9$
particles collapsed to solid connected particles of 0.2-0.4 μm after calcination at 950°C for twenty hours. Figure 4.2 is the micrograph of the calcined BaTi₄O₉. This clearly indicated that the spherical particles were hollow. Spray drying tends to generate powder with a hollow spherical structure. In the process of the drying, evaporation takes place quickly from the surface of solution droplet. A film of solute develops on the surface of the droplet when the concentration of the solution is high enough to precipitate. Then the liquid in the interior of the droplet will diffuse to the surface to evaporate, where the thickness of the film grows further.⁴¹,⁴⁵

The morphology of as-prepared BaTi₄O₉ was very different from that of as-prepared BaTiO₃. BaTiO₃ exhibited a finer but non-spherical particles (see Fig. 3.4). The cause of the difference could be due to spray drying and/or decomposition. For some solutes, the film formed is not strong and breaks during the drying.⁴⁵ It is also possible that the hollow spherical particle disintegrates during the combustive decomposition. Hydrated titania gel is an inorganic polymer which can gelatinize from TiO(NO₃)₂ solution at room temperature. It is more
Figure 4.2 Scanning Electron Micrograph of BaTi$_4$O$_9$ After Calcined at 950°C for Twenty Hours
cohesive than ionic Ba(NO$_3$)$_2$ during spray drying. Therefore, the amount of TiO(NO$_3$)$_2$ in the solution is believed to be the cause of the different structure in the powder.

4.2. Metastability of Pb$_{0.5}$Ba$_{0.5}$Ti$_4$O$_9$

The solubility of PbO as a substitution for BaO in BaTi$_4$O$_9$ has been measured, and a second phase will appear beyond that limitation at equilibrium.$^{13}$ Solid-state reaction at 1300°C was used for the sample preparation in that earlier study. The solubility was 8-10% depending on the methods of determination. No indications of any solid solution beyond this point were observed by this synthetic approach. This is indicative that Pb$_{0.2}$Ba$_{0.8}$Ti$_4$O$_9$ and Pb$_{0.5}$Ba$_{0.5}$Ti$_4$O$_9$ would be metastable, if it was possible to prepare them. TG/DTA runs using air as purge gas indicated that these compositions started losing weight around 1000°C. This loss was due to PbO becoming volatile above that temperature.

The metastability of these compounds, prepared by combustion synthesis, was tested by calcination and subsequent XRD measurement.
The XRD patterns of $\text{Pb}_{0.2}\text{Ba}_{0.8}\text{Ti}_4\text{O}_9$ and $\text{Pb}_{0.1}\text{Ba}_{0.9}\text{Ti}_4\text{O}_9$ remained unchanged after the samples were calcined at $900^\circ\text{C}$ for twenty four hours. On the other hand, the XRD of $\text{Pb}_{0.5}\text{Ba}_{0.5}\text{Ti}_4\text{O}_9$ began to change after the powder was calcined at $800^\circ\text{C}$ for two hours. It transformed into mixed patterns of $\text{BaTi}_5\text{O}_{11}$, $\text{PbTiO}_3$ and $\text{TiO}_2$ (rutile) after the powder was calcined at $900^\circ\text{C}$ for two hours. Figure 4.3 is the XRD of the powder, which shows the results of this conversion. The chemical reaction should be

$$2 \text{ Pb}_{0.5}\text{Ba}_{0.5}\text{Ti}_4\text{O}_9 \rightarrow \text{BaTi}_5\text{O}_{11} + \text{PbTiO}_3 + 2\text{TiO}_2.$$  \hspace{1cm} (7)

The XRD of $\text{Pb}_{0.5}\text{Ba}_{0.5}\text{Ti}_4\text{O}_9$ calcined at $700^\circ\text{C}$ for four hours did not change at all from that of the as-prepared powder. The attempt to determine the decomposition temperature by a DSC run did not yield a clear result. This can be either that the enthalpy of the reaction was too small to be detected, or that the reaction was not fast enough to observe by a DSC. The starting temperature of the decomposition appears to be between $700^\circ\text{C}$ and $800^\circ\text{C}$.

The instantaneous temperature in the combustion synthesis can be rather high, but the duration of time is very short. As a result, the
Figure 4.3 XRD result of $\text{Pb}_{0.3}\text{Ba}_{0.5}\text{Ti}_4\text{O}_9$

after Calcined at $900^\circ\text{C}$ for two Hours
"equivalent" annealing temperature/time in a combustion synthesis compared to that during a traditional solid-state reaction should be much lower. This effectively low temperature synthesis allows for greater metastability. Such equivalent low temperature is consistent with that the as-prepared BaTiO₃ containing some carbonate that must be removed by calcining at 800°C. On the other hand, a temperature of 800°C can hardly be expected to yield any product in the BaO-TiO₂ system for solid-state synthesis. BaTi₄O₉ was prepared at 1300°C in a conventional solid-state synthesis.¹³,¹⁴

The essence for the formation of a metastable product is to provide an intimately mixed state between solid reactants and to supply heat for the synthesis for a very short time. This avoids high temperature diffusion during solid-state reaction that would decompose a metastable compound. Vapor deposition is a frequently used physical method to mix solid reactants in an amorphous "lasagna" state for subsequent annealing.²⁵,³¹ Sol-gel, coprecipitation, and simultaneous hydrolysis are chemical methods for the same goal. BaTi₅O₁₁ that is stable only up to 1130°C was synthesized by the simultaneous
hydrolytic method.\textsuperscript{1} Metastable compounds CaTi\textsubscript{2}O\textsubscript{3} and CaTi\textsubscript{4}O\textsubscript{9}, which cannot be prepared by solid-state reaction, have been synthesized by the sol-gel method.\textsuperscript{80} Many metastable compounds have unique properties and great technique importance. To synthesize these compounds hinges on the availability of relevant processing technology.\textsuperscript{25}

The combustion method offers a good route to synthesize metastable compounds. Pb\textsubscript{0.5}Ba\textsubscript{0.5}Ti\textsubscript{4}O\textsubscript{9} synthesized by the method began to decompose around 800° C, which was less stable than BaTi\textsubscript{5}O\textsubscript{11}. Therefore, the method can be used to synthesize metastable compounds, which are stable only up to 800° C, like perhaps HgO or Tl\textsubscript{2}O based high-T\textsubscript{c} superconductors.\textsuperscript{31} One controversy in the synthesis of compounds in the BaO-TiO\textsubscript{2} system is the existence of BaTi\textsubscript{6}O\textsubscript{13} and compounds having a higher titanium to barium ratio. Although BaTi\textsubscript{6}O\textsubscript{13} has been reported as synthesized by quenching a melt having a 1:4 ratio of BaO and TiO\textsubscript{2},\textsuperscript{81} simultaneous hydrolytic decomposition of alkoxides of barium and titanium did not produce BaTi\textsubscript{6}O\textsubscript{13} or higher titanium to barium ratio compounds.\textsuperscript{1} It is,
therefore, interesting to use a new synthetic method to prepare these compounds again.

The syntheses of $\text{Pb}_{0.2}\text{Ba}_{0.8}\text{Ti}_4\text{O}_9$ and $\text{Pb}_{0.5}\text{Ba}_{0.5}\text{Ti}_4\text{O}_9$ did not contradict the previous work on the solubility of PbO in $\text{BaTi}_4\text{O}_9$.$^{13}$ Pb$_{0.2}$Ba$_{0.8}$Ti$_4$O$_9$ is likely to decompose at 1300°C of the solid-state synthetic temperature. The syntheses makes it possible to prepare the single phase ceramics by using hot pressing or low temperature sintering. However, these metastable ceramics cannot be prepared by solid-state reaction.

4.3. Crystal Lattice Constants in $\text{Pb}_x\text{Ba}_{1-x}\text{Ti}_4\text{O}_9$

Figure 1.3 shows the crystal structure of $\text{BaTi}_4\text{O}_9$. $\text{Pb}_x\text{Ba}_{1-x}\text{Ti}_4\text{O}_9$ (where $x$ is 0.1, 0.2 or 0.5) have the isostructure with lead partially substituted for barium in the crystal since they share the XRD pattern (see Fig. 2.7). As $\text{PbTi}_4\text{O}_9$ has never been synthesized, substitution of lead in barium position will destabilize the compound which has been discussed in last section. Figure 4.4 is a close-up on Fig. 2.7 that shows the shifts of XRD peak positions among $\text{BaTi}_4\text{O}_9$ and $\text{Pb}_x\text{Ba}_{1-x}\text{Ti}_4\text{O}_9$. 
Figure 4.4 XRD of BaTi$_4$O$_9$ and Pb$_x$Ba$_{1-x}$Ti$_4$O$_9$ at 2θ of 25-35
The crystal structure of BaTi$_4$O$_9$ is orthorhombic with a space group Pnmm.\textsuperscript{7,14} The XRD peaks for BaTi$_4$O$_9$ and Pb$_x$Ba$_{1-x}$Ti$_4$O$_9$ were indexed according to JCPDS card of BaTi$_4$O$_9$.\textsuperscript{14} Their lattice parameters were then refined by a least-squares procedure.\textsuperscript{52} All the diffraction data were taken in sequence to minimize inconsistency of the instrument. DMS (Diffraction Management System) 2000 Version 2.77 with the Scintag PAD5 powder diffractometer was used for the lattice refinement.

The lattice constants of BaTi$_4$O$_9$ and Pb$_x$Ba$_{1-x}$Ti$_4$O$_9$ are listed in Table 4.1 and plotted versus molar fraction of lead, x in Fig. 4.5. The plot shows that the dependencies of the lattice constants are linear with x. It is intuitive that the lattice constants are linear with the concentration of substituting lead, such an incident has been widely observed.\textsuperscript{4,82-84} It is known as the Vegard's law.\textsuperscript{4} The volume of the unit cell does not change as much as the lattice constants. It is due to the expansion of axes a and b with x is partially compensated by contraction of c axis. One axis expands at the price by contraction of another axis with temperature or the concentration of substituting ion
Figure 4.5 Lattice Constants of $\text{BaTi}_4\text{O}_9$ and $\text{Pb}_x\text{Ba}_{1-x}\text{Ti}_4\text{O}_9$. 
has been observed.\textsuperscript{72,84} However, the volume always increases with temperature.

Table 4.1 Lattice Constants and Volume of BaTi\(_4\)O\(_9\) and Pb\(_x\)Ba\(_{1-x}\)Ti\(_4\)O\(_9\).

<table>
<thead>
<tr>
<th>x</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>6.2896</td>
<td>14.5253</td>
<td>3.7954</td>
<td>346.74</td>
</tr>
<tr>
<td>0.1</td>
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4.4. Summary

The BaTi\(_4\)O\(_9\) and Pb\(_x\)Ba\(_{1-x}\)Ti\(_4\)O\(_9\) powders, as-prepared by combustion synthesis are carbonate free. They are hollow spherical particles with a diameter around 1 \(\mu\)m. Pb\(_{0.5}\)Ba\(_{0.5}\)Ti\(_4\)O\(_9\) which has never been synthesized before, is metastable. It starts to decompose when heated to 800°C and breaks down to BaTi\(_3\)O\(_{11}\), PbTiO\(_3\) and TiO\(_2\) eventually. Lattice constants have been determined based on powder XRD data. They vary linearly with the molar fraction of lead.
CHAPTER V

Conclusion and Prospective Work

5.1. Conclusion

A novel combustion synthesis procedure for the bulk syntheses of crystalline and finely divided BaTiO$_3$, BaTi$_4$O$_9$ and Pb$_x$Ba$_{1-x}$Ti$_4$O$_9$ (where $x$ is 0.1, 0.2 or 0.5) has been studied. The procedure should be applicable to the synthesis of other compounds in the BaO-TiO$_2$ system as well as doped and multicomponent BaO-TiO$_2$ based ceramic powders. Ba(NO$_3$)$_2$, Pb(NO$_3$)$_2$, TiO(NO$_3$)$_2$ and alanine are intimately mixed by spray drying a solution of them. The ratios of Ba(NO$_3$)$_2$, Pb(NO$_3$)$_2$ and TiO(NO$_3$)$_2$ are according to the desired products. Alanine serves as a readily oxidizable compound for the combustion procedure. Its amount and effectiveness is determined by a TG/DTA run that shows a one step major reaction. Combustion reactions, which
convert the spray dried materials to the products directly, occur when they are heated to around 300°C.

The as-prepared BaTiO₃ shows a good stoichiometric ratio between barium and titanium. A small amount of carbonate in the product can be eradicated by heating the powder at 900°C for an hour. The particle size has been characterized by various means and is comparable to BaTiO₃ prepared by other chemical methods. The powder has been dry-pressed without additives and sintered in a furnace of a TMA instrument. Three stages of sintering have been observed and the activation energy of the last stage of sintering has been measured by the Ozawa method to be 4.2×10⁶ J/mole. An activation energy for sintering BaTiO₃ had never been reported before. Densities, grain sizes and dielectric constants of the sintered pellets have been measured and correlated. The highest dielectric constant that has been obtained is 2680.

Pb₀.₂Ba₀.₈Ti₄O₉ and Pb₀.₅Ba₀.₅Ti₄O₉ have not been synthesized before and cannot be prepared by conventional solid-state reaction. Pb₀.₂Ba₀.₈Ti₄O₉ is stable upon heating until PbO becomes volatile.
Pb$_{0.5}$Ba$_{0.5}$Ti$_4$O$_9$ is metastable and starts to decompose at 800°C. Lattice constants for BaTi$_4$O$_9$ and Pb$_x$Ba$_{1-x}$Ti$_4$O$_9$ have been measured based on powder XRD data and lattice parameter refinement.

5.2. Prospective Work

There are two parts of prospective work based on this study. The first part is using the combustion synthesis to prepare other compounds in the BaO-TiO$_2$ system. The second part is to determine the optimal grain size of ceramics by hot pressing submicron powders prepared by the combustion synthesis.

I. Combustion Synthesis in the BaO-TiO$_2$ System

Ba$_2$TiO$_4$, BaTiO$_3$, BaTi$_2$O$_5$, Ba$_6$Ti$_{17}$O$_{40}$, Ba$_4$Ti$_{13}$O$_{30}$, BaTi$_4$O$_9$, Ba$_2$Ti$_5$O$_{20}$ and BaTi$_5$O$_{11}$ are eight compounds have been reported in the BaO-TiO$_2$ system. BaTi$_5$O$_{11}$ is stable only up to 1130°C and will decompose to BaTi$_4$O$_9$ and TiO$_2$ beyond the temperature. High temperature calcination at 1100-1300°C was reported necessary to obtain single phase BaTi$_4$O$_9$ by the simultaneous hydrolytic
decomposition method. The only reported low temperature synthesis before this research is sol-gel processing.

Single phase BaTi$_4$O$_9$ was prepared as easily as BaTiO$_3$ in the combustion synthesis. Metastable Pb$_{0.5}$Ba$_{0.5}$Ti$_4$O$_9$ has been first synthesized by the method. It began to decompose around 800°C and decompose to BaTi$_5$O$_{11}$, PbTiO$_3$ and TiO$_2$ eventually. Therefore, the combustion synthesis can be used to prepare metastable compounds such as HgO or Ti$_2$O based high-T$_c$ superconductors, that are stable only up to 800°C. One controversy in the synthesis of compounds in the BaO-TiO$_2$ system is the existence of BaTi$_6$O$_{13}$ and compounds having a higher titanium to barium ratio. Although BaTi$_6$O$_{13}$ has been reported, simultaneous hydrolytic decomposition of alkoxides of barium and titanium did not yield BaTi$_6$O$_{13}$ or higher titanium to barium ratio compound. It is of great interest to use a new synthetic method to prepare these compounds. The controversy is likely caused by the metastability of these compounds and the combustion synthesis is an appropriate method to prepare metastable compounds.
To synthesize other compounds in the BaO-TiO<sub>2</sub> system, both of reported and unreported, by the combustion synthesis is this part of prospective work.

II. Determination of Optimal Grain Size of Ceramics

It is well documented that the performance of an electronic ceramic device depends on its chemical composition, compositional homogeneity, density, and grain size. For BaTiO<sub>3</sub> and BaTi<sub>4</sub>O<sub>9</sub> based ceramics, alumina and silica are detrimental to their performance. On the other hand, some dopants and substitutions are desirable for a better performance. As a result, pure BaTiO<sub>3</sub> and BaTi<sub>4</sub>O<sub>9</sub> ceramics are rarely used without compositional modification.

For pure and homogeneous BaTiO<sub>3</sub> ceramic, its room temperature dielectric constant depends on the density and grain size. The dielectric constant can reach 5000 with high density and about 1 \( \mu \text{m} \) grain size. The performance of same ceramic but having a large grain size is less than a third of that. Grain size is an important factor for the performance and strength of electronic ceramics.
The dopants and substitutions that enhance the performance of BaTiO$_3$ are currently introduced by solid-state method. A solid-state process always generates coarse particles. The lack of submicron size BaTiO$_3$ based powder also made the study on the effect of grain size on performance impossible. As a result, the optimal grain sizes in these ceramics are undetermined.

The combustion synthesis can be used to prepare submicron, compositional modified BaTiO$_3$ and BaTi$_4$O$_9$ based powders. These powder are then hot pressed into ceramics with desired grain sizes. The performance of these ceramics can be measured and the optimal grain size will be determined.
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APPENDIX A

SOME APPLICATIONS OF THERMAL ANALYSIS TO FULLERENES
SOME APPLICATIONS OF THERMAL ANALYSIS TO FULLERENES

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Thermal analysis is a convenient means of characterizing the soot used as a source of the carbon clusters, the extracted mixture of fullerenes, and the individual clusters themselves. TG in an inert atmosphere will rapidly assay the volatile fractions, presumably the lower molecular weight clusters. TG in oxygen indicates a slight weight gain for the soots and clusters prior to their combustion.

DSC in oxygen is used to determine the heat of combustion for the separated C\textsubscript{60} and C\textsubscript{70} materials. The combustion occurs around 300°C for the clusters. There is a small exothermic peak before this which is attributed to the oxidation associated with the slight weight gain. The heats of combustion measured are \(-18.7\) and \(-21.0 \text{ kJ mol}^{-1}\) for the C\textsubscript{60} and C\textsubscript{70} respectively.

MS-EGA indicates the loss of small amounts of water and argon at temperatures around 250°C in vacuum and of solvent at about 350°C prior to sublimation.

Keywords: fullerenes, heat of combustion for C\textsubscript{60} and C\textsubscript{70}

Introduction

Tremendous interest has been generated in the carbon clusters based on the soccer ball style cage-like structures. These materials, commonly referred to as 'fullerenes', form a significant fraction (5-20%) of the carbon soot generated from the electrical arcing between graphite rods in a reduced pressure of Ar [1]. The fullerenes are separated from the soot by sublimation in an inert atmosphere or extraction with various organic solvents, e.g., benzene, toluene, etc. The individual clusters are then separated from each other via chromatography [2].

Mass spectrometric examination of various chromatographic fractions revealed the presence of many other fullerenes beyond the major components, C\textsubscript{60}.
Trichlorobenzene proved superior at extracting both more and a wider range of fullerenes from the soot. It appears [2, 3] that there is approximately 16 wt% of lower molecular weight fullerenes, which are very predominantly C_{60} and C_{70}, and 2% of higher molecular weight fullerenes, C_{98} to C_{212}. One other very interesting extractable species that has been observed [3, 4] is C_{70}O.

Results and discussion

Thermogravimetry (TG)

One of the major contributions of TG is to assay the potential yield of fullerenes in the various sources of soot. Figure 1 shows TG curves, taken at 20 deg-min\(^{-1}\) in flowing Ar that has been gettered with hot Ti, for graphite and two sources of soot. The graphite is stable to above 1200°C in this atmosphere. The lower fullerenes are volatile in the 600°C to 800°C range and the higher fullerenes become volatile at about a 1000°C. Clearly the soot, S1, made ‘in house’ has a higher content of the lower fullerenes than the commercial sample, S2. A

![TG curves in gettered flowing (100 ml·min\(^{-1}\)) Ar at 20 deg·min\(^{-1}\)](image)

Fig. A.1 TG curves in gettered flowing (100 ml·min\(^{-1}\)) Ar at 20 deg·min\(^{-1}\) for two sources of soot. a) S1, prepared at OSU by Dr. James V. Coe, et al. b) S2, purchased from Texas Fullerenes, Inc. c) S1, after extraction with benzene

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value of 15 wt% is typical of the reported values. The sample after extraction shows less weight loss but indicates that the initial extraction procedure was incomplete.

Milliken et al. [5], report TG data for C$_{60}$ in flowing N$_2$ and air. They indicate the onset of weight loss in N$_2$ at a heating rate of 10 deg·min$^{-1}$ is about 600°C. This seems consistent with the sublimation conditions proposed [1] for separation of >400°C in vacuum for some length of time. The most interesting aspect of TG results is that 4–5 wt% are lost in the temperature region of 400°C to 600°C prior to sublimation. It was suggested [5] that this weight loss is due to tenaciously held solvent, toluene, which does not desorb until 400°C and above. Such adducts can be formed, however, it is claimed that the presence of a catalyst, e.g., FeCl$_3$ or Br$_2$, is required during digestion with the solvent [6].

From the data of Millikan et al. [5], the onset of weight loss in air is about 400°C. This is approximately 200°C lower the onset of weight loss for graphite. The combustion process for C$_{60}$ was complete by 600°C. The rate of the combustion process, however, is highly dependent on the surface area and the accessibility of the oxygen to the carbon surface. Great variability, therefore, is to be expected from one investigation to the next.

The mixed C$_{60}$ and C$_{70}$ fraction from the OSU soot, S1, extracted with benzene was heated at 20 deg·min$^{-1}$ in gettered Ar and oxygen. The TG curves are presented in Fig. 2. There is a loss of several wt% in Ar below 600°C consistent

![TG curves](https://i.imgur.com/3Q5Q5Q.png)

**Fig. A.2** TG curves at 20 deg·min$^{-1}$ of a solid isolated from the benzene extract of the OSU soot (S1). a) In flowing (100 ml·min$^{-1}$) gettered Ar. b) In flowing (100 ml·min$^{-1}$) O$_2$
with Milliken et al. [5]. Unfortunately, the sample size was only 1.0 mg so that passing the exhaust into a heated FTIR cell was not sufficiently sensitive to determine the volatile species during any portion of the experiment. MS-EGA results are presented later which help to clarify the low temperature weight loss.

The combustion of the mixed sample in oxygen is interesting in that the small initial weight might be due to the formation of some oxides, such as the C_{70}O described earlier [3, 4]. The combustion process begins around 400°C for this sample under these experimental conditions. This is at a somewhat lower temperature than that observed by Milliken et al. [5], in air.

![Graph showing TG curves at 20 deg-min^{-1} in flowing (100 ml-min^{-1}) O_{2}. a) Graphite b) S1, Soot, OSU, J. V. Coe, et al. c) S2, Soot, Texas Fullerenes, Inc. d) S1, after extraction with Combustion of the raw materials is compared with graphite and a soot after extraction in Fig. 3. Graphite is clearly the most stable of the materials with respect to oxidation. The two soots behave similarly and also reveal the small weight gain attributed to formation of a solid oxide prior to the combustion. The soot after extraction is surprisingly reactive, presumably due either to an enhanced surface area and porosity or residual solvent.

**Evolved Gas Analysis (EGA)**

Samples of both soots and separated C_{60} and C_{70} materials, chromatographically isolated [7] from the extract of the OSU soot, were heated to 1000°C in an MS-EGA apparatus [8, 9] under vacuum, 10^{-6} Torr, at 20 deg-min^{-1}. In our earlier
results [10] on an unseparated extract, only water vapor was detected by the quadrupole MS up to 150 Daltons. Curves for C_{60} are presented in Fig. 4. There is in-

![Graph](image)

Fig. A.4 MS-EGA curve of water for C_{60} extracted from S1 heated in vacuum at 20 deg-min^{-1}

![Graph](image)

Fig. A.5 Simultaneous DTG and DTA curves for the extracted material heated in flowing (100 ml-min^{-1}) oxygen at 20 deg-min^{-1}

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dication of water and argon around 250°C. Around 350°C there are peaks in the 65 to 105 range indicative of some residual solvent. Similar results were observed for C\textsubscript{70} except that the temperature ranges were about 100°C lower. Further work is underway on these materials.

_Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC)_

The TG experiments in the previous section were performed by simultaneous TG/DTA using a Seiko, Model 5200 instrument. The TG curve for the oxidation of the C\textsubscript{60}-C\textsubscript{70} mixture shown in Fig. 2 was very closely paralleled by the exothermic DTA signal. The very close correspondence of the differential TG (DTG) curve and the DTA curve is indicated in Fig. 5. There is a clear indication of overlapping events, presumably the separate oxidation of the C\textsubscript{60} and C\textsubscript{70}.

This difference in oxidation rates offers another opportunity to assay the soots in advance for their contents of fullerenes. To more closely examine this possibility, the soots were examined by DSC and compared with graphite. The DSC curves determined in oxygen are shown in Fig. 6.

![DSC curves for various soots and graphite in flowing (100 ml\textperiodcentered min\textsuperscript{-1}) oxygen at 10 deg\textperiodcentered min\textsuperscript{-1}. a) Graphite b) S1, OSU soot c) S2, Texas Fullerenes, Inc. d) SAE, S1 soot after extraction with benzene](image)

*Fig. A. 6* DSC curves for various soots and graphite in flowing (100 ml\textperiodcentered min\textsuperscript{-1}) oxygen at 10 deg\textperiodcentered min\textsuperscript{-1}. a) Graphite b) S1, OSU soot c) S2, Texas Fullerenes, Inc. d) SAE, S1 soot after extraction with benzene
As predicted by the TG curves in Fig. 3 and the work of Millikan et al. [5], the exothermic peak associated with the graphite combustion occurs at a much higher temperature than for the soots. The area under the DSC curve for graphite gives an observed heat of combustion of \(-32.3 \text{ kJ g}^{-1}\). This is in excellent agreement with the reported value of \(-32.8 \text{ kJ g}^{-1}\) [11].

The combustion of the soots are virtually complete by the temperature that the graphite combustion begins. The DSC curve for the graphite is reasonably symmetrical, however, the curves for the soots suggest the presence of overlapping events. It is speculated that the lowest temperature process corresponds to the combustion of the fullerences and the heat from this process combined with higher surface areas of the soots initiates the combustion of the remaining soot at a relatively low temperature. It must be recalled that there is an initial weight gain observed for this process and the early portion of the DSC curve should reflect this event.

The measured heats of combustion for the three soots are much lower than for graphite. They are \(-26.6, -23.6, \) and \(-22.5 \text{ kJ g}^{-1}\) for the S1, S2, and SAE materials respectively. This implies a considerably lower heat of combustion for the fullerences or the volatilization of significant amounts of material. The reported enthalpy of sublimation for the lower fullerences is around \(233 \text{ J g}^{-1}\) [12]. Even in oxygen it may be possible for the material to volatilize sufficiently that the heat of combustion is not released within the confines of the DSC detector.

The DSC curves for the separated C\(_{60}\) and C\(_{70}\) are presented in Fig. 7. There are small exothermic peaks around 275°C which are attributed to the oxidation as-

---

**Fig. 7.** DSC curves for C\(_{60}\) and C\(_{70}\) extracted and separated from S1 and heated at 10 deg min\(^{-1}\) in flowing (100 ml-min\(^{-1}\)) oxygen.
sociated with slight weight gain described earlier. These amount to -0.3 to 
-0.5 kJ·g\(^{-1}\). The major oxidation peaks are asymmetrical beginning around 300°C 
and ending around 520°C. The heats of combustion of the C\(_{60}\) and C\(_{70}\) calculated 
from the areas are -18.7 and -21.0, excluding the small peak, and -19.1 and 
-21.5 kJ·g\(^{-1}\), when including the combined exotherms, respectively. While these 
heats are somewhat lower than those observed for the soots, they are still too 
large to explain alone the observed difference in the heat of combustion of the 
graphite and soots. Using the observed heats of combustion for graphite and C\(_{60}\), 
a value of -13.2 kJ·g\(^{-1}\) is calculated for the conversion of graphite to C\(_{60}\).

Conclusion

Thermoanalytical methods are a powerful, relatively fast, and versatile class 
of techniques. TG is particularly suitable for assaying the relative fullerence con­
tents of soots. At this time neither TG nor DSC is able to clearly resolve the relative 
amounts of C\(_{60}\) vs. C\(_{70}\). The TG curves show a small weight gain in oxygen 
 prior to the combustion of carbon suggesting the formation of an oxide. It would 
be interesting to halt a TG curve at that point and measure the C\(_{70}\)O content by 
chromatographic methods.

Sealed containers may be necessary to accurately measure the heat of combus­
tion of the fullerenes because of their volatility. The combustion of the soots ap­
pears virtually complete by the temperature that normal graphite begins to 
oxidize. The fullerenes and soots adsorb significant moisture during normal 
storage and this is probably responsible for most of the low temperature weight 
loss in an inert atmosphere. There are, however, small amounts of argon and sol­
vents incorporated into these materials.

Thermal analysis will continue to play a major role in the characterization of 
these interesting materials and the processes in which they are involved.

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7 S. Olesik, to be published.


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APPENDIX B

A STUDY OF THE EFFECT OF PURITY ON THE USE OF NICKEL
AS A TEMPERATURE STANDARD FOR THERMOMAGNETOMETRY
A STUDY OF THE EFFECT OF PURITY ON THE USE OF NICKEL AS A TEMPERATURE STANDARD FOR THERMOMAGNETOMETRY


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d TA INSTRUMENTS, INC., 109 LUKENS DR., NEW CASTLE, DE 19720, USA

Samples of nickel, varying by four orders of magnitude in their purity, were studied by thermomagnetometry (TM), to determine if the extrapolated end point ($T_c$) changes. $T_c$ is virtually identical for the 99.99 and 99.999% samples. Samples of less purity did show changes.

Simultaneous DTA/TM can accurately define $T_c$ by comparing with the melting points of pure metals determined simultaneously. The melting points of lead and zinc bracket the $T_c$ for nickel. They were added to the sample pan prior to TM of nickel. Experiments were performed at heating rates in the range from 1 to 20 deg min$^{-1}$. It serves as a pilot study for the ICTAC Committee for Standardization to more accurately define the recommended values of $T_c$.

Keywords: Ni as a temperature standard, thermomagnetometry

Introduction

Faster experimental turn-around times can be achieved in TG by using smaller furnaces that will heat and cool more rapidly. This requires a smaller sample to assure a homogeneous temperature throughout the sample zone. It also places greater demands on the precise placement of the temperature sensor in order to correspond with the sample temperature. This concern led to the proposal by Noren et al. [1], to use magnetic materials in the exact position of the sample and utilize the transformation temperature, $T_c$, from the ferri or ferromagnetic form to the paramagnetic one to calibrate the true sample temperature more accurately.
They indicated that several magnetic materials could be run simultaneously and proposed a series of pure metals and alloys to cover the temperature range 100°–1000°C. This suggestion was adopted immediately by others [2] using this type of instrumentation. The strength of the magnetic field gradient necessary to achieve a measurable effect is low and can be provided by an inexpensive, small, permanent magnet. In fact a high magnetic field is undesirable for this purpose [3]. Comparisons of such standards with others have been made over the intervening years [4–6].

The Standardization Committee of ICTAC conducted a detailed program and round-robin, under the direction of Garn, Menis, and Wiedemann, to establish nickel and four magnetic alloys as standards for the comparison of temperature in TG [7]. This effort culminated in the availability of these materials through N.I.S.T. [8].

Although individual participants in the program had relatively good precision, there was a wide range of results reported from one laboratory and/or type of instrument to another. These are described in detail in Refs [7] and [8]. As an example, the range of reported values for nickel was 345°–363°C with an average of 354.4°C.

Recommended values ranged from 354° [1] to 361°C [9].

The advent of modern simultaneous TG/DTA instrumentation provides an opportunity to re-evaluate these magnetic transitions using the melting points of pure metals for direct comparison [6]. Metals can be selected whose melting points bracket the magnetic transition and whose temperatures of melting form the basis for the practical realization of the current international temperature scale [10]. Both melting and the magnetic transitions can be measured simultaneously on the same instrument using the identical temperature sensor.

This paper presents the results of a brief pilot study by the Task Group on Magnetic Standards of the Committee for Standardization of ICTAC. It represents the combined efforts of five laboratories in North America, Europe, and Asia using instruments from four different manufacturers. One laboratory was chosen to utilize high-sensitivity DTA in place of TM to determine the values of $T_c$.

The study has three basic goals: 1) to determine the feasibility of obtaining accurate results with a high degree of interlaboratory agreement, 2) to evaluate the effect of heating rate on the results in order to set the proper protocol for a much larger and broader study, 3) to establish the degree of purity that is required for the standard materials, and 4) to compare the values of $T_c$ obtained by TM and DTA. Nickel was selected for this initial study.

**Experimental procedures and results**

Wires of lead and zinc having a purity of 99.99 wt% or better were obtained along with foils of nickel having purities of 99, 99.9, 99.99, and 99.999 wt% from Goodfellows, Inc. Approximately 5 mm x 5 mm samples of nickel were cut from a
single piece of foil. Several foil samples of each purity and a length of each wire were distributed to the participants.

Experimental protocol called for a flow of inert gas (argon or nitrogen) at the flow rate normally used by the investigator for that apparatus. Each sample was to be heated briefly above $T_c$ and cooled once prior to taking any data for record [1]. This anneal made no significant difference, based on a few checks that were made. The sample was to be placed in good thermal contact with the sample pan. A magnetic field gradient adequate to note the effect without being excessive was to be used. Samples of lead and zinc were to be placed alongside the nickel. Sample sizes were left to each investigator depending upon the particular instrument used. Prior temperature calibration of the instrument was deliberately not specified. One laboratory (C) purposely did not calibrate the instrument in advance in order to test the calibration algorithm more extensively.

Each purity was to be run at 10 deg min$^{-1}$. A second series was to be run at nominally 1.0, 2.5, 5.0, 10, and 20 deg min$^{-1}$ using a sample of the highest purity. Each investigator was asked to make several runs using the same set of conditions in order to evaluate their reproducibility. The types of apparatus used in this study were two Seiko model TG/DTA 320, Stanton Redcroft model STA 1500, TA Instruments model SD2960, and MAC Science HT-TG/DTA.

![Simultaneous TM/DTM/DTA curves for Ni, Pb, and Zn at 20 deg min$^{-1}$ in Ar (Lab A)](image-url)
Table B.1 Measured values of melting temperatures of Pb and Zn, and measured and corrected values for magnetic transition temperature, Tc, of Ni, having different purities, from simultaneous TM/DTA in an inert gas at 10 deg/min' $T^m$ = measured, $T^c$ = corrected, Lab. = code Data from Lab. E are based entirely on DTA (see text)

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<th>$T^m_{Zn}$</th>
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</table>

A typical set of simultaneous TM/DTM/DTA curves is presented in Fig. 1. Extrapolated onsets are used to determine the observed melting temperatures for lead and zinc. $Tc$ was measured as the extrapolated end point based on both the TM and DTA curves. The end point is used for $Tc$ as the loss of magnetism defines the transition temperature [3]. The DTA results proved more sensitive to the extrapolated end point (about 0.2° to 0.4°C) than TM. Hence, the values reported for $Tc$ are derived from DTA.

The difference between the observed melting point and the defined values [10] (419.527°C zinc, 327.5°C lead) was used for calibration. A linear interpola-

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tion between these correction factors was used to determine the correction factor applied to the observed magnetic transition temperature for each experiment. The results are summarized in Tables 1 and 2 for the DTM and DTA measurements.

Table B.2 Measured values of melting temperatures of Pb and Zn, and measured and corrected values for magnetic transition temperature, $T_c$, of Ni, 99.999 wt%, from simultaneous TM/DTA in an inert gas at the indicated heating rates. $T_m^\text{m}$ = measured, $T_c^\text{c}$ = corrected, Lab. = code Data from Lab. E are based entirely on DTA (see text)

<table>
<thead>
<tr>
<th>H.R. deg min$^{-1}$</th>
<th>Lab.</th>
<th>$T_{\text{Pb}}^\text{m}$ / °C</th>
<th>$T_{\text{Zn}}^\text{m}$ / °C</th>
<th>$T_{\text{Ni}}^\text{m}$ / °C</th>
<th>$T_{\text{Ni}}^\text{c}$ / °C</th>
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The same correction procedure was used for the values of $T_c$ obtained by DTA. A typical DTA experiment is shown in Fig. 2. The peak temperature of the DTA excursion was used to establish $T_c$ on the basis that the process was over at that point and the return to baseline was controlled by instrumental factors.

The trends in corrected $T_c$ with heating rate for both the DTM and DTA methods are presented in Fig. 3.

Discussion

Limitations of space preclude an extensive discussion of the results and only the major issues and conclusions are described here.

Comparison of the DTA with the DTM results indicates that the $T_c$ based on the peak temperature of the DTA excursion is consistently lower (about 0.7°C) in temperature at all heating rates and sample purities. The implication is that the selection of the peak temperature for $T_c$ is probably incorrect. The selection of the return to baseline will obviously lead to an increase in the reported DTA temperatures and better agreement with the DTM results.

Values of $T_c$ based on DTM show a very high degree of reproducibility among the different laboratories. In Table 1, for the highest purity, the spread of values is

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Fig. B.2  Simultaneous DTA curves for Ni, Pb, and Zn at 10 deg.min$^{-1}$ in N$_2$ (Lab E)
only ±0.2°C, consistent with the reported values of σ. Values throughout Tables 1 and 2 are generally within 2σ. This degree of agreement between several laboratories is vastly superior to the results of the earlier round-robin [7]. Clearly the use of simultaneous TM/DTM/DTA is an excellent way to define the value of $T_c$ and has direct correspondence with the International Temperature Scale.

The method has the added advantage of largely removing the dependency of $T_c$ on the heating rate. Unfortunately, only three laboratories reported their results as a function of heating rate and one of these is based on DTA results. The results, however, reveal very little change with heating rate over the range reported. The trends are inconsistent as seen in Fig. 3. Apparently the shift in melting points, used as calibration, provides an adequate correction for the lag induced by increased heating rates.

A minimum purity of 99.99 wt% seems to be required for this source of nickel. Naturally, the absolute purity required depends on the specific impurities present. Iron or cobalt will raise the value of $T_c$ but other impurities lower it. Apparently there is significant iron or cobalt in the 99.9 wt% sample and much greater quantities of other impurities in the 99 wt% specimen.
A greatly expanded program will redetermine the magnetic transition temperatures for the metals and alloys currently used to calibrate the temperature axis in TG and TM. These preliminary results clearly demonstrate that a substantial improvement, perhaps an order of magnitude reduction in the uncertainty, can be expected and also provide some basis for selecting the purity of the materials.

References

8  N.I.S.T. Certificate GM 761 ICTA Certified Reference Materials for Thermogravimetry, N.I.S.T., Gaithersburg, MD.

Zusammenfassung — Zur Bestimmung der Änderung von \( T_C \) wurden mittels Thermomagnetometrie (TM) Nickelproben untersucht, die sich ihrer Reinheit nach über vier Größenordnungen unterscheiden. Für 99.99% und 99.999% Proben sind die Werte für \( T_C \) scheinbar identisch. Proben mit geringerem Reinheitsgrad zeigen Abweichungen.

APPENDIX C
THE THERMAL EXPANSION AND STABILITY
OF KTiOAsO₄ AND RELATED COMPOUNDS
The thermal expansion and stability of KTiOAsO₄ and related compounds

Z. Zhong, P.K. Gallagher*, D.L. Loiacono and G.M. Loiacono

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Crystal Associates, Inc., Waldwick, NJ 07463 (USA)

(Received 20 October 1992; accepted 3 February 1993)

Abstract

KTiOAsO₄ and related compounds are of interest because of their electro-optical properties. The thermal stability of the material is important both for its potential use as a device and in determining suitable conditions for its crystal growth. The stabilities and melting points of M TiO AsO₄, where M is K, Rb or Cs, and selected combinations thereof, have been investigated in oxygen and nitrogen using simultaneous thermogravimetry-differential thermal analysis (TG-DTA). The melting temperatures were observed to correlate with the ionic radius of M⁺.

The materials are highly anisotropic and the thermal expansion of KTiOAsO₄ is reported over the temperature range from −170 to 950°C based on thermodilatometry (TD) of an oriented single crystal. The second order phase transformation at 861°C was much more evident in TD than in DTA.

INTRODUCTION

The compounds, KTiOP O₄ (KTP) and its isomorphs, have received considerable attention for second harmonic generation (SHG). The analogous arsenate compound KTA has shown particular promise because of its higher figure of merit and electro-optical coefficients combined with an increased stability at higher powers [1].

Single crystals have been grown from molybdate and tungstate fluxes [2]. Knowledge of the decomposition temperatures and phase equilibria are essential for this process. The melting temperatures, decomposition temperatures, and any solid-solid phase transformations are of particular

* Corresponding author.

1 Dedicated to Hans Georg Wiedemann. It is a pleasure for PKG to take part in honoring an old friend and respected colleague who has contributed so much to thermal analysis over many years.
relevance. Simultaneous TG–DTA techniques are used herein to study these phenomena in both oxygen and nitrogen. Oxidation reduction processes associated with the arsenic ion should introduce into these equilibria a dependence on the partial pressure of oxygen.

The crystal structure is orthorhombic at room temperature (point group \(mm^2\), space group \(Pnma\) (\(C_{m}^{2}\) \(Z = 8\)) [3, 4]. The unit cell is composed of chains of very slightly distorted \(\text{AsO}_4\) tetrahedra sharing oxygen ions with somewhat more distorted \(\text{TiO}_6\) octahedra. The \(M^+\) ions fill voids in this structure.

Such a structure should have a highly anisotropic thermal expansion. In fact, cracking along the \(c\) axis has been a problem during crystal growth. This has been attributed to differences in thermal expansion between the crystal and the platinum suspension wires [2]. Consequently, the thermal expansion of an oriented single crystal of \(\text{KTiOAsO}_4\) is measured over a wide temperature range from \(-170\) to \(950^\circ\text{C}\) using TD.

EXPERIMENTAL PROCEDURES AND RESULTS

Single crystals of \(\text{MTiOAsO}_4\) (where \(M\) is \(K\), \(Rb\) or \(Cs\)) were grown by the high temperature solution (HTS) method from tungsten based solvents, as previously reported [2]. Typical crystal growth parameters were, initial growth temperature \(950-910^\circ\text{C}\), temperature lowering rate of \(2^\circ\text{C}\) per day, and seed rotation rate of \(30\ \text{rev min}^{-1}\). For the mixed crystals, the initial melt composition was prepared at a \(1:1\) mole ratio; however, X-ray diffraction analyses showed that the crystal compositions were \(K_{0.5}Rb_{0.5}\text{TiOAsO}_4\) and \(K_{0.85}Cs_{0.15}\text{TiOAsO}_4\). The crystal grown from the \(Rb_{0.5}Cs_{0.5}\text{TiOAsO}_4\) composition was not analyzed. Samples of these crystals were crushed and lightly ground in an agate mortar prior to thermal analysis. A cube approximately \(0.5\ \text{cm}\) on edge was carefully cut, oriented by X-ray, and polished from a single crystal of \(\text{KTiOAsO}_4\) for the thermal expansion measurements.

Simultaneous TG–DTA measurements were performed using a Seiko Model 320 System. Nominally \(15\ \text{mg}\) samples were heated at \(10^\circ\text{C}\ \text{min}^{-1}\) in flowing oxygen or nitrogen at approximately \(100\ \text{ml min}^{-1}\). Typical curves are presented in Fig. 1 for \(\text{KTiOAsO}_4\). The melting and decomposition temperatures were measured from the extrapolated onsets of the processes and are summarized in Table 1 for all of the materials.

The thermal expansion measurements used the Perkin-Elmer System 7 TMA module. The sample was heated at \(2^\circ\text{C}\ \text{min}^{-1}\) in a slow flow of helium. The data were collected in two separate experiments covering different ranges of temperature. The first covered the low temperature range from \(-170\) to \(160^\circ\text{C}\) and the second the range from \(30\) to \(950^\circ\text{C}\). Data were collected for each of three crystallographic directions. The data are
Table C.1

Decomposition and melting temperatures for alkali substitutions in MTiOAsO$_4$ (extrapolated onset temperatures in oxygen and nitrogen)

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<tr>
<th>M</th>
<th>Oxygen</th>
<th>Nitrogen</th>
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<tbody>
<tr>
<td></td>
<td>Dec./°C</td>
<td>Melt./°C</td>
</tr>
<tr>
<td>K</td>
<td>1156</td>
<td>1137</td>
</tr>
<tr>
<td>K, Rb</td>
<td>1164</td>
<td>1114</td>
</tr>
<tr>
<td>Rb</td>
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</tr>
<tr>
<td>K, Cs</td>
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<td>1095</td>
</tr>
<tr>
<td>Rb, Cs</td>
<td>1140</td>
<td>1062</td>
</tr>
</tbody>
</table>

presented in Fig. 2 without correction for the small amount of thermal expansion due to the fused quartz holder.

The change in slope associated with the second order ferroelectric transformation near 86°C is evident, particularly in the c axis data. Hence, the data were fit in two separate temperature regimes, before and after this transition. The fit of $\Delta L/L_{294}$ to third order polynomials as a function of temperature is summarized in Tables 2 and 3. The second order polynomial describing the linear coefficient of thermal expansion can be derived by simple differentiation of these third order polynomials.
Fig. C.2 Thermal expansion for single crystalline KTiOAsO₄ at 2°C min⁻¹ in helium.

**TABLE C.2**

A fit to the thermal expansion of KTiOAsO₄, over the temperature range -170 to 800°C:

\[ \Delta L/L_{298} = a + bT + cT^2 + dT^3 \]

where \( T \) is the temperature in kelvin

<table>
<thead>
<tr>
<th>Axis</th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
<th>( d )</th>
</tr>
</thead>
<tbody>
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<td>(1.12511 \times 10^{-4})</td>
<td>(-4.6042 \times 10^{-12})</td>
</tr>
<tr>
<td>( \parallel ) B</td>
<td>(-2.5298 \times 10^{-3})</td>
<td>(5.98544 \times 10^{-6})</td>
<td>(9.66804 \times 10^{-9})</td>
<td>(-3.6037 \times 10^{-12})</td>
</tr>
<tr>
<td>( \parallel ) C</td>
<td>(-4.0622 \times 10^{-4})</td>
<td>(3.51577 \times 10^{-5})</td>
<td>(-5.8902 \times 10^{-9})</td>
<td>(-2.1710 \times 10^{-12})</td>
</tr>
</tbody>
</table>

**TABLE C.3**

A fit to the thermal expansion of KTiOAsO₄ over the temperature range 900-950°C:

\[ \Delta T/L_{298} = a + bT + cT^2 + dT^3 \]

where \( T \) is the temperature in kelvin

<table>
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<tr>
<th>Axis</th>
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<th>( d )</th>
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<tr>
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<td>(-5.4428 \times 10^{-4})</td>
<td>(4.87860 \times 10^{-7})</td>
<td>(-1.4574 \times 10^{-10})</td>
</tr>
</tbody>
</table>

Figure 3 shows an indication of the degree of fit, in this case, for the \( a \)-axis data. Every thirtieth datum point is indicated to enhance the legibility. Again the data are uncorrected for the very small expansion of the sample holder.
DISCUSSION

The stability of KTiOAsO₄ in oxygen is greater than in nitrogen by approximately 100°C as determined by the onset of mass loss in Fig. 1. Table 4 is a summary of the calculated mass losses based upon various products. The observed final mass (37 mass %) is considerably less than that predicted by the vaporization of arsenic(III) oxide and oxygen alone (52.5 mass %). It is however more than that predicted by the formation of TiO₂ as the only residue (33.0 mass %).

This suggests the presence of some ill-defined potassium titanate approaching the composition K₂Ti₁₀O₂₁. This is not inconsistent with the phase diagram presented in Fig. 4 [5]. The residue at that point would be in the two phase field of K₂Ti₁₀O₂₁ + TiO₂ and very near the pure TiO₂ boundary. The phase diagram also shows that the incorporation of arsenate into the simple potassium titanate compound raises the melting point nearly 200°C.

A strong minimum in the DTG curve occurs near the mass loss associated with the complete loss of arsenic but prior to the loss of potassium. The specific details or sequence of the loss of oxygen, arsenic,

<table>
<thead>
<tr>
<th>TABLE C.4</th>
<th>Mass loss calculations for KTiOAsO₄</th>
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<tr>
<td>Compound</td>
<td>Mass loss/%</td>
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<tr>
<td>KTiO₂ₓ</td>
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<tr>
<td>KₓAs₂Ti₁₀O₂₁</td>
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</table>
and potassium from KTiOAsO₄ cannot be established without further X-ray diffraction work or evolved gas analysis.

The incongruent melting point of KTA at about 1130°C is clearly evident in the DTA curve shown in Fig. 1. The ferroelectric transition with an onset around 861°C, which is pronounced in earlier dielectric measurements [1], is marginally detectable in the DTA trace. This transition appears to be of

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**Fig. C.4** The partial phase diagram for the system K₂O-TiO₂.

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**Fig. C.5** Melting temperatures of M₅TiO₃AsO₄ compounds as a function of the average ionic radius of M⁺.
second or higher order, generating only a step in the baseline as a result of the change in heat capacity without a change of enthalpy. It is best determined through dilatometry as is shown later.

The melting temperatures in Table 1 show a correlation with the average ionic radii of the M+ ion as shown in Fig. 5. The two data points for mixed but adjacent ions fit well; however, the point for the K$_{0.85}$Cs$_{0.15}$ compound in oxygen has a significantly lower melting temperature than would be predicted solely on the basis of their average ionic radii.

The thermal expansion behavior is similar to that of other ferroelectric materials such as LiNbO$_3$ [6]. A ferroelectric phase transition reported at 880°C, which is pronounced in earlier dielectric measurements, is marginally detected in the DTA data presented in Fig. 1. The transition appears to be of second or higher order, generating only a small step in the baseline as a result of a change in heat capacity without a change in enthalpy. The transition is better defined in the thermal expansion curve taken parallel to the c axis. The onset appears at 861°C in agreement with a value of 852°C recently reported [7].

If a single domain single crystal were desired, it would be necessary to impose the electrical field around 900°C and maintain it during cooling to near room temperature. Subsequent heat treatments would be limited to below 850°C in order not to depole the crystal.

REFERENCES