

# A New Binder for Nano-Materials

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## **ABSTRACT**

A lot of effort is put in the preparation of nano-materials to make them available for applications. The properties of these nano-powders are different from the regular ones. Nano-particles typically have size between 5 to 100 nm. The sintering temperatures of these particles are lower than the conventional ones. In order to investigate the first stage of sintering we need a binder, which can hold these nano-particles together providing it with good strength.

## **INTRODUCTION**

Ceramics is one of the three large classes of solid materials (ceramics, metals, polymers). The word ceramics comes from the Greek word *keramos*, which means 'pottery'. However, the term ceramics originates from Sanskrit where it means 'to burn'. Ceramic is an inorganic, non-metal material, which are usually produced using clays and other crystalline in nature minerals like alumina, silicon nitride, Silicon carbide etc. Ceramics are used for the production of bricks, cement, tiles, and glass. It is also used for

insulators, semiconductors, superconductors, magnets, aerospace shuttle surfaces, etc. It helps decrease pollution, capture toxic materials and convert hydrocarbons and carbon monoxide from dangerous gases into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Today's catalytic converters in vehicles are made of cellular ceramics and help convert noxious hydrocarbons and carbon monoxide gases into non-toxic carbon dioxide and water.<sup>1,2</sup>

There are two basic ways of ceramic processing: wet powder processing and dry powder processing. In wet powder processing, powder is mixed in liquid and cast into the green body before firing. In dry powder processing, which is the subject of this project, dry powder is pressed in the green body and then fired. Binders are the most important additives of the ceramic sintering process. A binder is a material, used to hold particles together and provide mechanical strength or to ensure uniform consistency. Not all binders are suitable for all types of powders processed. The binder selection depends on the viscoplastic properties required for the particular fabrication process, the type of casting surface (porous, nonporous), process temperatures, and stability of properties with respect to long-term storage. The function of the binder is to impart sufficient strength to the ceramic product, to add elastic properties, which are important for handling and shaping of the material during the post forming stage. There are binders for aqueous systems and for non-aqueous (organic solvent) systems. The first type consists of colloidal types, carbohydrate derived organics, and non-carbohydrate derived organics. The most common binders in the second type are: Polyvinyl butyral, Polyvinyl formal, Polymethylmethacrylate. The binders used in this experiment are Methacrylic acid, glacial and Poly (Propylene Carbonate). They both need to be dissolved in organic solvents – respectively methanol and acetone.

Besides the addition of binders to the Barium Titanate powder, there are some other important processes in the preparation and in the processing of the powder. One of them is hydrothermal synthesis, which is used to synthesize  $\text{BaTiO}_3$  out of  $\text{TiO}_4$  and  $\text{BaCl}_2$ . Hydrothermal synthesis is defined as the treatment of aqueous solutions or suspensions of precursors at elevated temperature and pressure. Another important process is the sintering of the powder. This process is usually used to form complex shapes, to produce alloys, or in the preliminary molding of ceramics or glass powders into forms that can be permanently fixed by firing. In fact, during sintering, small particles of metal are welded together by applying heat at temperatures below the melting point.<sup>3</sup>

## **PURPOSE**

The purpose of this research is to find a better and a stronger binder for nano-particles. The product for which the binder is used should be difficult to break after binder burnout and after sintering. Furthermore, the binder should have a relatively low decomposition temperature, so that the first stage of sintering could be studied – if the temperature of burnout of the binder is bigger or equal to that of the first stage of sintering, it would be impossible to distinguish between the effect of the binder and the effect of the sintering process. The properties that the binder gives to the ceramic product are to be examined through various analyses as DSC, the surface area and through density measurements.

## **EXPERIMENTAL**

### **Powder synthesis**

The environment in which BaTiO<sub>3</sub> is prepared needs to be basic; that is why a 2N NaOH solution is prepared by solving 40g NaOH pellets into 0.5l distilled water.

For the preparation of BaTiO<sub>3</sub>, TiCl<sub>4</sub>, BaCl<sub>2</sub>.2H<sub>2</sub>O and NaOH are necessary. 13ml of TiCl<sub>4</sub> with density 1.726g/ml is available, so the quantity of BaCl<sub>2</sub>.2H<sub>2</sub>O needs to be calculated.

In order to achieve the optimal ratio between Ba and Ti  $n(\text{BaCl}_2 \cdot 2\text{H}_2\text{O}) = 1.6 * n(\text{TiCl}_4)$

$$n(\text{TiCl}_4) = m/M_w;$$

$$m(\text{TiCl}_4) = V * \text{density};$$

$$n(\text{TiCl}_4) = V\rho/M_w = (13 * 1.726)/189.67 = 0.12 \text{ gmol};$$

$$m(\text{BaCl}_2 \cdot 2\text{H}_2\text{O}) = n * M_w = 0.192 * 244.23 = 46.89 \text{ g}.$$

### **Hydrothermal Synthesis**

180 ml cold distilled water is poured into the glass reactor. 13ml TiCl<sub>4</sub> is very slowly poured in the water and the mixture is stirred. 46.89gms BaCl<sub>2</sub>.2H<sub>2</sub>O is added and the mixture is stirred again. 390ml NaOH is added to provide the basic environment and stirred. The mixture is put in the reactor and it stays there for 8 hours at temperature 100°C. Cold water is periodically added to the cold-water reservoir so that the cold-water condenser functions properly.

### **Centrifugation**

Then centrifuge the BaTiO<sub>3</sub> got from the above reaction in a centrifuge. It is important to have the same volume of content (BaTiO<sub>3</sub>) in all the centrifugal tubes for the proper working of the centrifugal force. Turn on the centrifuge and keep it on maximum speed for

five minutes. After this is done, throw away the water ( $\text{BaTiO}_3$  gets coagulated at the bottom because it has five to six times density larger than water). Repeat this procedure two more times. Then add water once again this time mixing well and pouring it in two-glass bowls.

### **Drying in the vacuum furnace**

After centrifugation, wet powder is put in two glass bowls (not in one, but in two, so that the evaporation surface is larger). The bowls are placed in the vacuum furnace and they remain there for 12 hours at  $85^\circ\text{C}$ . After the process is over place the powder in two separate bottles and then in a desiccators.

## **Powder Processing**

### **Green-body formation**

From the powder produced, four portions of 3 grams each are taken. The first portion is mixed with a binder: 0.15 grams Methacrylic acid, glacial and 3ml Methanol. It is milled in a quartz bowl until it dries, and then it is split into six portions of 0.5grams each. These portions are pressed in the press machine (at 250 Mpa, for one minute).

In the second 3grams portion 0.15 grams of Polypropylene Carbonate is added along with 6 ml of acetone. The mixture is milled until it is completely dry, and then it is pressed in the portion of 0.5 grams in the press machine for one minute at the pressure of 250Mpa.

The third portion is not mixed with anything. It is only split in portions of 0.5 grams and pressed. The fourth portion is mixed with 5ml of distilled water. Then milled well until dry and pressed. The tablets produced are called green bodies.

Table 1: The characteristics after the binder burnout process

<b>Material</b>	<b>After process:</b>	<b>Annotations</b>	<b>Characteristics</b>
$\text{BaTiO}_3$	Binder burnout at $350^\circ\text{C}$	Binder=Methacrylic acid, glacial+ methanol	Grayish (as oxygen escaped)
$\text{BaTiO}_3$	Binder burnout at $800^\circ\text{C}$	Binder=Poly(Propylene carbonate) + acetone	White
$\text{BaTiO}_3$	Binder burnout at $350^\circ\text{C}$	Only $\text{BaTiO}_3$ powder	White
$\text{BaTiO}_3$	Binder burnout at $350^\circ\text{C}$	$\text{BaTiO}_3$ powder + water	White

## **Sintering**

After the binder burnout process, the green bodies were placed in a tube furnace at 1300 degrees Celsius for two hours.

## **Characterization**

### **Density**

After sintering, find the density of the tablets by Archimedes principle and by dimension measurement and weight.

### **DSC**

The operation of the DSC is based on measurement of the thermal response of an unknown specimen as compared with a standard, when the two are heated uniformly at a constant temperature.

### **Surface area**

A (Nitrogen) gas adsorption technique was used to determine the surface area of the sintered pellets.

Surface area is the area of a given surface. Roughly speaking, it is the "amount" of a surface, and has units of distance squared per gram.<sup>4</sup>

### **SEM.**

The Scanning Electron Microscope, or SEM, is a tool for seeing the unseen worlds of micro space.<sup>5</sup>

The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution

## **RESULTS:**

Table 2: Density of the tablets after binder burnout

<b>Material</b>	<b>Annotations</b>	<b>Average density (g/cm<sup>3</sup>)</b>
BaTiO <sub>3</sub>	Binder=Methacrylic acid, glacial + methanol	2.734
BaTiO <sub>3</sub>	Binder=Poly (Propylene carbonate) + acetone	2.645

The density of the tablets without any binder cannot be measured because they are too fragile.

Table 3: Density (by Archimedes principle), surface area and characteristics of the tablets after sintering:

<b>Material</b>	<b>Annotations</b>	<b>Surface area (m<sup>2</sup>/gr)</b>	<b>Density (g/cm<sup>3</sup>)</b>	<b>Characteristics (after sintering)</b>
BaTiO <sub>3</sub>	Binder=Methacrylic acid, glacial+ methanol	Couldn't find because of time limitation	5.666	Broken a little
BaTiO <sub>3</sub>	Binder=polypropylene carbonate + acetone	9.2	5.640	Not broken at all
BaTiO <sub>3</sub>	No binder, only powder	9.1	5.832	Broken a lot
BaTiO <sub>3</sub>	Powder with water only	9.2	5.787	Broken a little

Table 4: Observation during processing

<b>PROCESS BINDER</b>	<b>Body Green Formation</b>	<b>After Binder Burnout</b>	<b>After Sintering</b>
Methacrylic Acid, Glacial	Relatively easy to work with: mill and clean the instrument	Gray in color	Relatively easy to break.
Poly (Propylene Carbonate)	Easy to work with: mill and clean the equipment	No visible change	Relatively hard to break.
Powder only	Hard to work with: mill and clean the equipment.	No visible change	Very easy to break.
Water	Very hard to work with: mill and clean the equipment, it's sticky.	No visible change	Very easy to break.

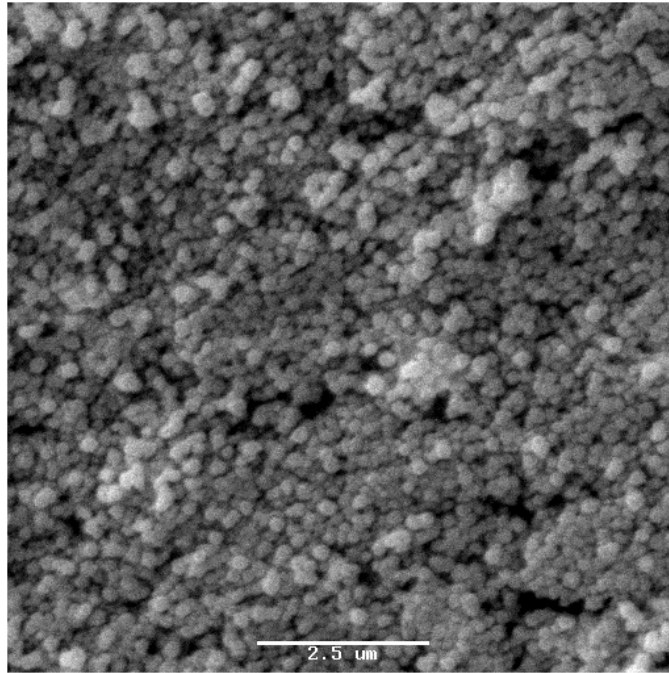


Fig. 1: SEM image of BaTiO<sub>3</sub> with Poly (Propylene Carbonate) after binder burnout at 350°C

### *DSC analyses*

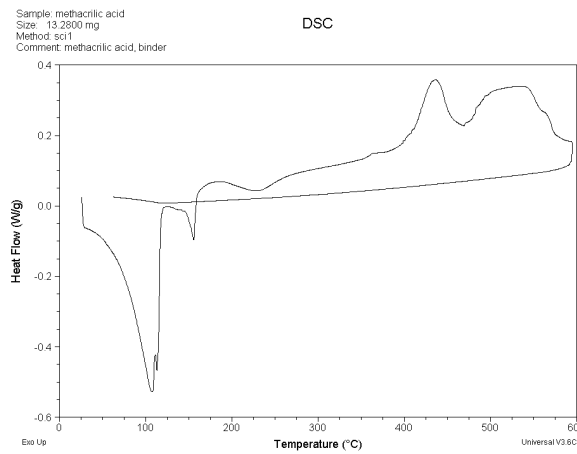


Fig 2: Methacrylic acid, Glacial  
Decomposition  $T^0 = 550\text{ }^{\circ}\text{C}$

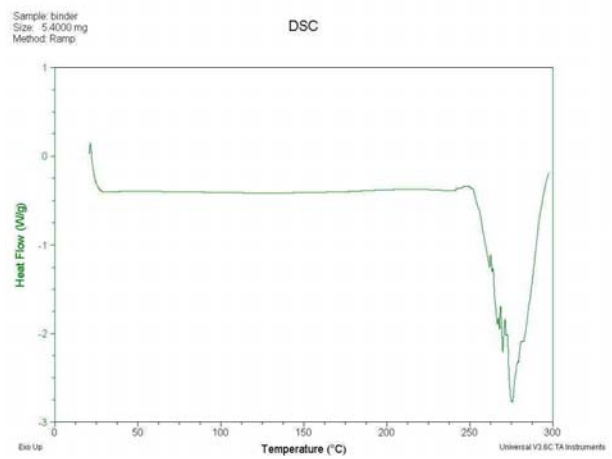


Fig. 3: Poly(Propylene Carbonate)  
Decomposition  $T = 275\text{ }^{\circ}\text{C}$

## DISCUSSION

Four different samples of BaTiO<sub>3</sub> with different binders or no binder at all are used for comparison. The first sample of BaTiO<sub>3</sub> is mixed with Methacrylic acid, glacial. This binder is attempted because it is frequently used in lab works. Poly (Propylene Carbonate) is the second binder and it is used because it has low decomposition temperature. Both Methacrylic acid, glacial and Poly (Propylene Carbonate) are polymers and possess the properties of the organic polymer binders. The third sample is powder with nothing at all. It is used in comparison with the other binders, and because it would be cheapest and easiest to produce ceramics without any additional organic substances. Water is used because it has a very low decomposition temperature (it boils at 100°C), and it is freely available and no organic residue is left in the powder.

During green body formation the easiest sample to work with is the one with Poly (Propylene Carbonate). It does not stick to the molder, and after the pressing it takes no effort to clean the molder. It is much harder to break than the others both after burnout and after sintering. The density of the product is almost unaffected by the different materials used as binders. There is a very little difference between the densities of the two samples with polymer binders, which is negligible: the density of the sample with Methacrylic acid is 2.734 g/cm<sup>3</sup> and the density of the other sample is 2.645 g/cm<sup>3</sup>. As for after sintering, the sample with no binder has the highest density, and the densities of the samples with polymer binders are almost the same – the differences are again negligible. The surface area also appears to be unaffected by the different binders used in the experiment, because the surface area of the sample with Poly (Propylene Carbonate) and the surface area of the sample with water are equal – they both are 9.2 m<sup>2</sup>/g, and the surface area of the powder only sample is 9.1 m<sup>2</sup>/g. This is not an important difference. The DSC analyses of the two binders show that the decomposition of Methacrylic acid, glacial occurs in three stages – this can be seen in figure 2, where the line representing the decomposition of the binder makes three peaks. Methacrylic acid, glacial has a decomposition temperature of 550°C (figure 2), that is much higher than the decomposition temperature of Poly (Propylene Carbonate), which is about 275°C (figure 3). The grains of the sample with Poly (Propylene Carbonate) can be seen in the picture above – there are not many agglomerations, and the grains are almost all the same size and shape, which contributes to the good quality of the material.

## **CONCLUSIONS**

Our goal was to find a binder, which would provide the nanomaterials viscosity and strength. After all the tests and referring to tables 2, 3 and 4 we come to the conclusion that Poly (propylene carbonate) is the most appropriate binder, because it can hold dry powder aggregates together while sintering, burning out cleanly, uniformly while providing good strength to sintered parts. Not enough with this it is able to decompose at a low temperature.

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