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A new family of $ATiO_3$ (A=Ba, Ca, Sr,) shape formed nanomaterials for a non thermal plasma catalytic application

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Introduction

In the last years, research in plasma technology has been largely increased for the treatment of exhaust gas flow. The use of a catalyst allows enhancing the efficiency of the system. In the so-called packet bed reactors, the presence in the plasma zone of materials with high dielectric properties such as $BaTiO_3$ compound[1], allows to accumulate charges. The formation of DBD plasma type is thus favored for a lower voltage compared with an empty reactor. Simultaneously, numerous works deal with the properties of the $BaTiO_3$ due to the world development of multilayer ceramic capacitors based on this material. A large part of the research concerns the synthesis by various methods especially by wet chemicals ones using several precursors[2]. Despite its high cost for materials synthesis, the sol-gel process became attractive for advanced ceramics with high purity and homogeneity. To improve at low temperature, the dielectric properties, some researches are focused on others materials such as $CaTiO_3$.

Another way of research concerns the shape forming of powder catalysts. Various shape types exist in catalysis processes such as extrudates, monoliths or balls. Even so, each morphology should be related to reactor dimensions and to the gas flow passing through the reactor. In a plasma catalytic reaction, balls comply with these properties. To prepare spherical pellets, the selected procedure was based on the combination of oil-drop granulation with sol-gel route, as already developed in our group[3] for the preparation of alumina-silica materials. During the granulation process, drops of sol are put through a paraffin oil layer. After aging in an aqueous solution, the soft wet-gel particles became rigid. In this work, the goal is to use the sol-gel method to prepare at low temperature, the $ATiO_3$ family (A= Ca, Sr, Ba) from titanium alkoxide and alkaline earth acetate precursors. We present also the opportunity to transpose the oil-drop process to the shape forming of dielectric spherical pellets able to be used in a non thermal plasma reactor.

Materials and Methods

The starting solutions of alkaline earth acetate precursors were prepared in glacial acetic acid as solvent. After complete dissolution, a solution of titanium (IV) diisopropoxide (in isopropanol) was dripped into the alkaline earth acetate solution in stochiometric proportions. After evaporation of the excess of solvent, an orange gel was obtained whatever the nature of the alkaline earth. To optimize the shape forming, some additives as Butvar-B98, methylethylketone and ethylmethacrylate were added to the sol. Balls were obtained by oil-drop procedure using a column containing two layers of 15 cm of mineral oil (upper layer) and 5 cm of concentrated aqueous ammonia solution (lower layer), respectively. After 1 hour of aging the balls were washed with ethanol in order to remove traces of oil or ammonia.
Whatever the shape of the materials (powder or balls), they were dried in a ventilated oven at 80°C for 12 hrs and finally annealed at 800°C during 2hrs in static air.

Results and Discussion

The XRD patterns of $ATiO_3$ (Ca, Sr, Ba) powders materials show only the formation of a single perosvkite phase (Fig.1, $BaTiO_3$ pattern) after annealing. The weight loss deduced from thermal gravimetric analysis (Fig. 2) confirms that the annealing temperature (800°C) is enough to form the perovskite structure in agreement with previous works[2].

As additives, the Butvar-B98 compound acts as a binder, the methylethylcetone (MEK) and ethylmethacrylate (EMC) as a wetting and a dispersion medium, respectively. The best mechanical strength of the balls with a diameter size of 1.8 mm was obtained with 1.9 wt% of B98, 1.9 wt% of MEK and 0.7 wt% of EMC without modification of the perovskite structure (Fig. 1 oil-drop). Whatever the shape, the crystallites sizes of around 20 nm corresponding to grains size comprise between 0.1 µm and 10 µm which are in aggregated form. This feature has been confirmed by BET measurements giving respectively 10 $m^2.g^{-1}$ and 12 $m^2.g^{-1}$ for $BaTiO_3$ and $CaTiO_3$ compounds. The first test in plasma reactor is encouraging; the balls resist to the application of high voltage and to mechanic shocks between balls and reactor due to the flow.

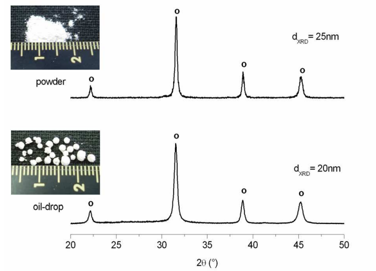

Figure 1. XRD patterns of powder and ball of $BaTiO_3$ (800°C; 2 hrs). (PDF file :79-2263)

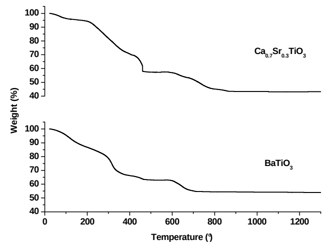

Figure 2. Thermogravimetric curves of $Ca_{0.7}Sr_{0.3}TiO_3$ and $BaTiO_3$ dried powders.

The use of sol-gel method has revealed the possibility to prepare at relatively low temperature, a new nanomaterials family ($ATiO_3$) in two shapes, powder and balls with similar properties. Moreover, the additives used are efficient to strengthen the micro-structure of perosvskite type.

Significance

This work based on the sol-gel shape forming process of dielectric materials displays significance for an industrial application in a plasma packed-bed reactor. Moreover, this method allows varying the composition of alkaline earths on the $ATiO_3$ perovskite structure.

References

1. Ruixing, L., Quing Tang, S.Y., and Tsugio,S., *Fuel Processing Technology*, 87, 617 (2006).
2. Pithan, C., Shiratori, Y., Waser, R., Dornseiffer, J., and Haegel, F., *J.Am.Ceram.Soc.*, 89, 2908 (2006).
3. Amariei, D., Rossignol, S., and Kappenstein, C., *Advance in Sciences and Technology*, 45, 2089 (2006).