Rheological Characterization of BaTiO₃ Sol-Gel Transition

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Abstract. BaTiO₃ gels were prepared by hydrolysis and polycondensation reactions between titanium isopropoxide and barium hydroxide in presence of methoxyethanol, methanol and water. The rheology of the sol-gel transition was studied with a rheometer allowing low amplitude sinusoidal oscillations. Experimental data show a continuous increase in the complex viscosity along with time, showing the progressive character of the transition. The influence of synthesis operating variables was studied. The gelation time, which definition is based on viscoelastic measurements, increases exponentially when the water content is increased, when the dilution due to the methoxyethanol is reduced or when the temperature is lowered. Different growth models were used for the characterization of the particles in the solution. These models suggest that the polymerisation first produces spherical particles (mass fractals) and that these spherical particles then agglomerate to form a linear network.

Keywords: rheology, sol-gel, barium titanate

1. Introduction

Barium titanate is a material widely used by the electronic ceramics industry, due to its high dielectric constant. Industrial synthesis of barium titanate powders is made through solid state reactions between barium carbonate and titanium oxide. This process has a relatively low cost despite the required high temperature (1100°C). But its main disadvantage is that the homogeneity of the final product strongly depends on the milling. In the sol-gel process, the synthesis is made in solution, which enables to obtain a good mixing of the reactants at molecular scale. It is therefore possible to obtain a better homogeneity and crystallinity of the material after calcination. Several methods of preparation of barium titanate using the sol-gel route have been developed. These methods essentially differ by the nature of the barium precursor: hydroxide, alkoxide or acetate [1–5].

This work completes three anterior studies on BaTiO₃ sol-gel synthesis. Lemoine et al. [6] studied the reaction mechanism during the synthesis based on titanium isopropoxide, barium hydroxide, methoxyethanol and water. Pirard et al. [7] and Lecloux et al. [8] studied the porous texture (specific surface area, porous volume, dimension and shape of the pores) and the crystallization of the powders synthesized by the same method.

Besides BaTiO₃ powders, the sol-gel process enables the easy synthesis of thin films, which could lead to the realization of very high capacity condensators. However, making BaTiO₃ thin films by dip-coating requires an advanced knowledge of the rheology of the sol-gel transition in order to control the thickness and regularity of the film with precision [9–11]. Rheological measurements concerning the sol-gel transition can be found in the literature, but mainly for silica [12–17], not for BaTiO₃.
During visco-elastic measurements, perturbation or rupture of the growing network, which could be due to too large movements of the measurement cell, must be avoided. The measurement procedure used in this work complies to this restriction by the use of very low amplitude oscillations, thus of very weak resulting strain [16-17]. The originality of this process is based on the automatic adaptation of the applied stress in order to obtain the desired strain amplitude.

Besides the indispensable informations for specific uses of gels (thin layers, or fiber making), rheological studies also allow some investigations on the sol-gel transition mechanisms.

The goal of the present work is the characterization of the rheological behaviour of the gelling solutions according to synthesis operating variables: evolution of the gelation time and of the viscosity. The analysis of the shape of the growing particles will also be carried out according to different growth models [15, 17, 18].

2. Experimental Procedure

2.1. Sample Preparation

All chemicals were of the highest commercially available purity. Titanium isopropoxide (Ti-(O-iso C3H7)4) and 2-methoxyethanol were obtained from Janssen Chimica, barium hydroxide monohydrate from Aldrich and methanol from Merck.

The sample preparation was conducted under nitrogen flow and the solutions were sheltered from moisture and CO2 to avoid precipitation of titanium hydroxide or barium carbonate. The four reagents were mixed under vigorous stirring at room temperature in an Erlenmeyer flask first conditioned under nitrogen flow. They were added in the following order:

- 2-methoxyethanol, stabilizer of the titanium alkoxide towards water,
- titanium isopropoxide (Stirring time: 15 minutes),
- solution of barium hydroxide monohydrate (Ba(OH)2·H2O) in methanol (C = 0.735 mol/l) (Stirring time: 10 minutes),
- solution of water in methanol (C = 10.84 mol/l) (Stirring time: 1 minute).

The relative quantities of each reagent depend on the desired gel composition. This composition can be described by three operating variables:

- the Ba : Ti mole ratio, which is always set to 1 : 1 in the realised trials,
- the 2-methoxyethanol/Ti mole ratio, called \(M\), which varies from 3.5 : 1 to 6 : 1,
- the water : Ti mole ratio, called hydrolysis ratio \(H\), which varies from 6 : 1 to 9.5 : 1.

The value of the hydrolysis ratio \(H\) takes into account the water content of the barium hydroxide monohydrate.

The mixture obtained is immediately transferred to the rheometer measurement cell.

2.2. Experimental Method

Rheological measurements are carried out using a Bohlin CS10 rheometer equipped with a measurement cell made up of concentric cylinders (“Double Gap 40/50 mm”, capacity 30 ml). The moving part is subjected to sinusoidal oscillations of 0.1 Hz frequency and which amplitude is controlled in order to obtain a 0.1% strain at maximum in the analysed mixture. Perturbation of the gelling by the measurement cell is then avoided.

Instant measurement of the applied stress allows the calculation of the complex modulus \(G^*\) (which is the ratio stress/strain taking into account the phase angle \(\delta\) between these quantities). Other quantities can be derived: the elastic modulus \(G' = |G^*| \cos \delta\), the viscous modulus \(G'' = |G^*| \sin \delta\) and the complex viscosity \(\eta^* = |G^*|/2\pi f\), where \(f\) is the frequency of the oscillations. The evolution of these quantities is followed along with time.

The measurement cell is maintained at a constant temperature using a thermostatic bath. Measurements were taken at 25°C, except those which were used to study the influence of temperature.

2.3. Sample Identification

The sample identification takes into account the synthesis operating variables. So, a sample with a mole ratio \(M\) of 4 : 1 and an hydrolysis ratio \(H\) of 8 : 1 which is analyzed at a temperature \(T\) equal to 25°C is identified by \(M4H8T25\).

3. Results

The gelation time is defined as the amount of time elapsed between the addition of the last droplets of