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ANALYSIS OF SOL EVOLUTION IN SOL-GEL SYNTHESIS BY USE OF RHEOLOGICAL MEASUREMENTS

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Lucrarea tratează aspecte referitoare la sinteza sol-gel a titanatului de bariu prin metoda acetat, utilizând ca precursori principali acetatul de bariu şi izopropoxidul de titan. Prin adăugare de apă solul format devine mai viscos şi se transformă intr-o structură de tip gel. Această comportare se datorează intensificării reacţiilor de hidroliză şi policondensare, fapt ce conduce la o creştere a gradului de policondensare. Viscozitatea dinamică a solului s-a determinat experimental pe baza măsurătorilor de tensiune şi viteză de forfecare. S-a propus un model reocinetic pentru calculul viscozităţii solului în funcţie de timp şi de cantitatea de apă adăugată.

The paper focuses on characterization of barium titanate sol-gel synthesis by acetate method, starting from barium acetate and titanium isopropoxide as main precursors. The formed sol becomes more viscous and evolves towards a gel structure by addition of water. This is due to an enhancement of hydrolysis and polycondensation reactions, producing an improvement of polycondensation degree. Measurements of shear stress and shear rate were performed to determine the sol dynamic viscosity. A rheokinetic model was proposed to estimate the sol dynamic viscosity depending on operating time and water amount.

Keywords: barium titanate, perovskites, sol-gel synthesis, rheokinetic model

1. Introduction

Sol-gel synthesis is widely employed to obtain metal oxides starting from a chemical solution (*sol*), usually containing a metal alkoxide dissolved in a solvent, which undergoes hydrolysis and polycondensation reactions and evolves towards an integrated two-phase network (*gel*) [1].

Hydrolysis of an alkoxide $M(OR)_n$, wherein M is a metal (Al, Ce, Cr, Mo, Si, Sn, Ti, Zr, Zn, W) and R represents an alkyl group, consisting in substitution of alkoxyl groups (–OR) with hydroxyl groups (–OH), is shown in Scheme 1:

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$$\begin{array}{l} M(OR)_n + H_2O \rightarrow M(OR)_{n-1}(OH) + ROH \\ M(OR)_{n-1}(OH) + H_2O \rightarrow M(OR)_{n-2}(OH)_2 + ROH \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ M(OR)_{n-(x-1)}(OH)_{x-1} + H_2O \rightarrow M(OR)_{n-x}(OH)_x + ROH \\ \hline M(OR)_n + x\,H_2O \rightarrow M(OR)_{n-x}\,(OH)_x + x\,ROH,\ 1 \le x \le n \end{array}$$

Scheme 1

High values of alkoxyl ligands number, metal ions number and alkyl group dimension enhance the hydrolysis rate [1]. Hydrolysis does not produce the appearance of large polymer molecules therefore it occurs without a changing of medium viscosity.

Polycondensation of metal hydroxides formed by hydrolysis implies oxolation and alkoxolation reactions. An oxolation reaction takes place between two hydroxyl groups (–OH) and leads to the forming of M–O–M bonds, determining an increase of polymer molecular mass and crosslinking degree till a gel tridimensional structure is obtained. In the same way acts the alkoxolation reaction which implies a hydroxyl group (–OH) and an alkoxyl group (–OR). Due to the polycondensation reactions, the medium viscosity increases and the sol evolves towards the formation of a gel, which is a viscoelastic material containing both a liquid phase and a solid phase.

A series of oxolation and alkoxolation reactions corresponding to metal hydroxides polycondensation is illustrated in Scheme 2:

$$(RO)_{n-1}M–OH + HO–M(OR)_{n-1} \rightarrow (RO)_{n-1}M–O–M(OR)_{n-1} + H_2O$$
$$(RO)_{n-1}M–O–M(OR)_{n-1} + HO–M(OR)_{n-1} \rightarrow (RO)_{n-1}M–O–M(OR)_{n-2}–O–M(OR)_{n-1} + ROH$$
$$(RO)_{n-1}M–O–M(OR)_{n-2}–O–M(OR)_{n-1} + HO–M(OR)_{n-1} \rightarrow \ldots \rightarrow \text{gel}$$

Scheme 2

All the hydrolyzed species $M(OH)_x(OR)_{n-x}$ ($1 \le x \le n$) are present within the sol obtained by hydrolysis. Each of these species represents a monomer which generates its own polycondensation chain.

Rheokinetic model

A rheokinetic model describing the dynamics of sol viscosity is proposed. Assuming that the sol contains a single monomer and the polycondensation reaction occurs according to a second-order rate law, the reaction rate can be expressed by means of differential equation (1), wherein c_{mn} represents monomer concentration, k_{pc} is polycondensation rate constant and τ expresses elapsed time [1]:

$$-\frac{dc_{mn}}{d\tau} = k_{pc} c_{mn}^{2} \tag{1}$$

By separation of variables and integration of differential equation (1), the integrated rate law (2) is obtained, wherein c_{mn0} is initial monomer concentration:

$$c_{mn} = \frac{c_{mn0}}{1 + c_{mn0} k_{pc} \tau} \tag{2}$$

Correlation (2) links monomer conversion, X, and polycondensation degree, N, to time, initial monomer concentration and polycondensation rate constant:

$$X = 1 - \frac{c_{mn}}{c_{mn0}} = 1 - \frac{1}{1 + c_{mn0} k_{pc} \tau} \tag{3}$$

$$N = \frac{1}{1 - X} = 1 + c_{mn0} k_{pc} \tau \tag{4}$$

In case of polymerization by polycondensation, experimental researches proved that the momentary dynamic viscosity of the medium, η, is a power function with respect to polycondensation degree, N [2]:

$$\eta = K N^{\alpha} \tag{5}$$

Substituting equation (4) into equation (5), the correlation (6) expressing time evolution of sol dynamic viscosity is obtained:

$$\eta = K (1 + c_{mn0} k_{pc} \tau)^{\alpha} \tag{6}$$

According to the theoretical considerations concerning the rheology of polymer nonreactive solutions, α=1 till a critical value of polymer concentration and α=3.4 for concentration values larger than critical value [2].

Substituting $\tau = 0$ into equation (6) and considering that $\eta=\eta_0$ at $\tau=0$, wherein η_0 is the initial sol viscosity, the value of constant K becomes:

$$K = \eta_0 \tag{7}$$

Equations (6) and (7) lead to a rheokinetic model (8) based on two parameters (k_{pc} and α):

$$\eta = \eta_0 (1 + c_{mn0} k_{pc} \tau)^{\alpha} \tag{8}$$

Experimental observations evidenced that the hydrolysis agent accelerates the polycondensation reactions [1]. For this reason the polycondensation rate constant in equation (8) is multiplied by an exponential function with respect to hydrolysis agent concentration, c_{hd}, and a rheokinetic model (9) based on three parameters (k_{pc}, α and χ) is proposed:

$$\eta = \eta_0 \left[1 + c_{mn0} k_{pc} \exp(\chi c_{hd}) \tau\right]^{\alpha} \tag{9}$$

An experimental investigation consisting in characteristic rheokinetic measurements of barium titanate sol-gel synthesis was performed to identify the model parameters [3].

Barium titanate synthesis

Barium titanate ($BaTiO_3$) is one of the best known and widely used perovskites for electric ceramics due to its dielectric, ferroelectric, piezoelectric and pyroelectric properties. Multilayer ceramic capacitors, semiconductors with positive temperature coefficient, pyroelectric detectors, piezoelectric actuators, ultrasonic transducers, thermal switches, volatile and non-volatile memories are some of its applications.

$BaTiO_3$ can be obtained as powder [4-13], thin film [5, 9, 14-17], monolite [18], nanorod [19], fibre [20], its quality depending on synthesis route and involved precursors.

Synthesis methods of $BaTiO_3$ have been intensively investigated in the last time. Accordingly, fine particles can be produced in dry state by calcining of a mixture of barium carbonate or barium oxide and titanium oxide or by wet-chemistry techniques, including sol-gel, sol-precipitation, chemical co-precipitation or hydrothermal synthesis. Thin films were prepared by vacuum evaporation, sputtering, laser ablation, hydrothermal synthesis or sol-gel processing.

The sol-gel techniques offer advantages over other fabrication methods such as low processing temperature and investments costs, respectively high homogeneity and purity of obtained product. Controlling the rates of hydrolysis and condensation reactions, a precipitate, a gel or a stable colloidal solution can be obtained. A homogeneous gel state can be achieved by hydrolysis enhancement, respectively by lowering of solution temperature and also by addition of solvents like acetic acid, acetylacetone or 2-methoxyethanol [5, 8, 14, 16, 18].

Various methods were employed to prepare $BaTiO_3$ sols, the main precursors being a barium reagent and a titanium alkoxide. Acetate method is the most common sol-gel synthesis route, the involved precursors being barium acetate usually dissolved in acetic acid and an alkoxide such as titanium isopropoxide [4,5,14,18,20], titanium isobutoxide [14,15,19], titanium tetraethoxyde [8,9,17], titanium bis (ammonium lacto) dihydroxide [9] or titanium diisopropoxide bisacetylacetonate [10]. The hydrolysis was activated by water addition. Titanium alkoxides such as titanium isopropoxide or isobutoxide are usually sensitive to air moisture. Therefore they have to handle under inert atmosphere or modify by reaction with acetylacetone [10]. $BaTiO_3$ was obtained also by hydroxide method, using $Ba(OH)_2 \cdot 8H_2O$ and a titanium alkoxide as main precursors [4,8], by alkoxide method, adding titanium isopropoxide in a mixture obtained by dissolution of barium metal in dry isopropanol [4], or mixing a barium alkoxide, a titanium alkoxide, solvents and water [11,16,18].

This paper focuses on a qualitative and quantitative characterization of barium titanate sol-gel synthesis by acetate method.

2. Experimental

Reagents and apparatus

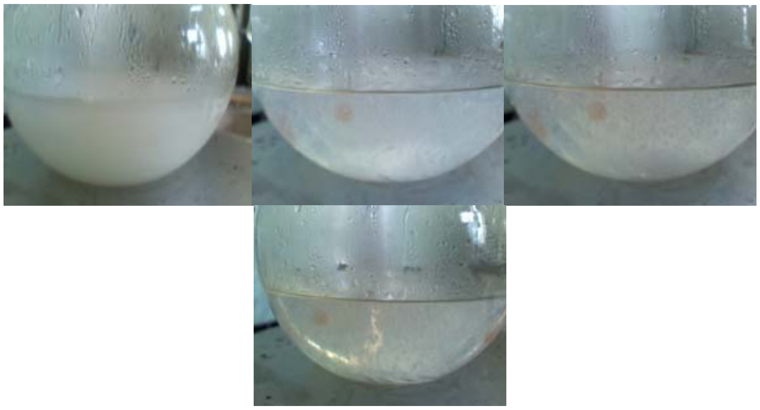
Anhydrous barium acetate, glacial acetic acid, titanium isopropoxide and isopropanol of analytical purity were employed to prepare $BaTiO_3$ sol.

Rheological measurements, consisting in determination of sol shear stress depending on shear rate, were performed with a CVO Bohlin Instruments rheoviscosimeter.

Procedure

The procedure was as follows. 8.5 g barium acetate was dissolved in 35 mL acetic acid in a Berzelius glass. The mixture was warmed for complete dissolution, cooled to room temperature and poured into a flask containing a prepared solution of 9.34 g titanium isopropoxide in 35 mL isopropanol. The homogeneous solution was stirred for 1 h then activated by slow addition of hydrolysis agent (distilled water). The obtained sol with whitish appearance was refluxed under continuous stirring and rheological measurements were achieved at 1 h, 2 h, 3 h and 4 h.

Experiments corresponding to various amounts of water (0.55 mL, 0.70 mL, 0.85 mL, 1 mL and 1.15 mL) were carried out. The sol rapidly turned into a glassy gel in the last experiment (Fig. 1). The sol state immediately after addition of water is illustrated in Fig. 1 a. It is observed that this whitish sol turns into a transparent and more viscous one in a few minutes (Fig. 1 b, c) and a glassy gel is obtained in 5 min (Fig. 1 d). An analysis of sol rheological behaviour was not possible in this case.



a **b** **c** **d**

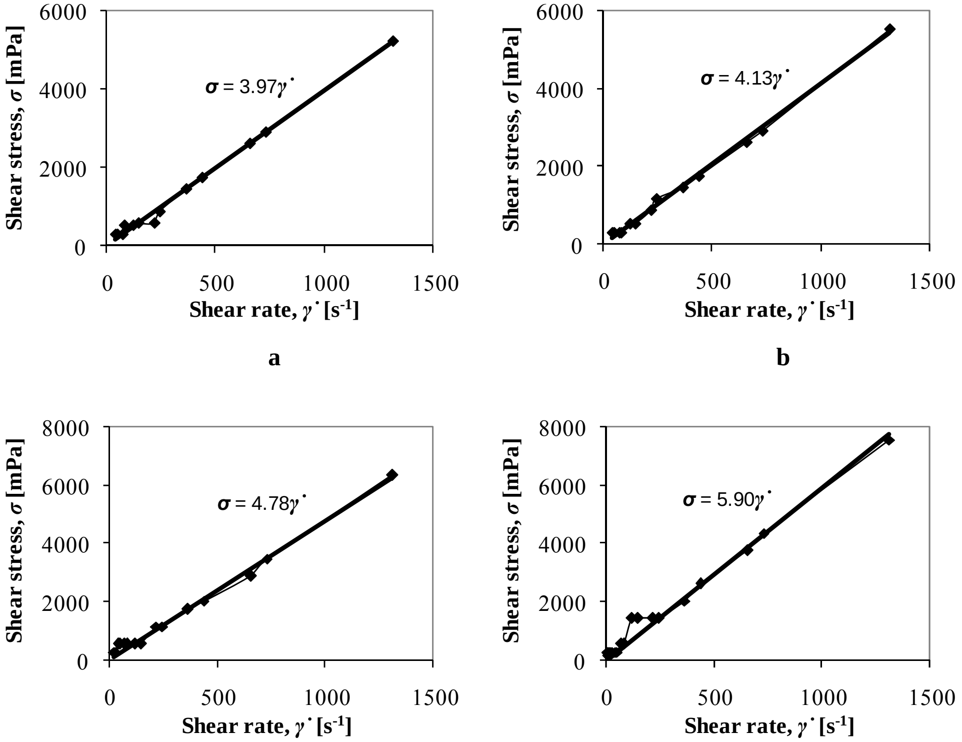
Fig. 1. Dynamics of gelation process for a volume of 1.15 mL water
(**a.** τ=0 s, **b.** τ=180 s, **c.** τ=240 s, **d.** τ=300 s)

3. Results and discussion

Graphic representations shown in Fig. 2 illustrate variation of sol shear stress, σ, versus shear rate, $\dot{\gamma}$, for an operating time of 4 h and various values of hydrolysis agent concentration, c_{hd}, which represents water mass divided by titanium isopropoxide mass.

A linear dependency between shear stress and shear rate is observed, so that the sol can be considered a newtonian fluid with dynamic viscosity, η, given by the straight line slope:

$$\eta = \frac{\sigma}{\dot{\gamma}} \text{ [mPa·s]} \tag{10}$$



a b

c d

Fig. 2. Variation of sol shear stress versus shear rate for τ=14 400 s and various values of hydrolysis agent concentration, c_{hd} (**a.** 0.059 g/g, **b.** 0.075 g/g, **c.** 0.091 g/g, **d.** 0.107 g/g)

Experimental data listed in Table 1 emphasize the influence of operating time and hydrolysis agent amount on sol dynamic viscosity. It is obvious that sol viscosity increases in time. It is also noticed that it increases with water concentration at any value of operating time, because an enlargement of water amount accelerates hydrolysis and polycondensation reactions, which leads to an enhancement of polycondensation degree and sol viscosity.

Data presented in Table 1 were employed to identify the characteristic parameters values of rheokinetic model (9). Minimizing the objective function described by relation (11), wherein c_{mn0}=0.25 g/mL and η_0=1.2 mPa·s, the following values of model parameters were regressed: k_{pc}=3.12·10^{-4} mL/g·s, α=0.89 and χ=13.80. The obtained values accord with those reported in literature [1].

$$f(k_{pc},\alpha,\chi)=\sum_{i=1}^{4}\sum_{j=1}^{4}\left\{\eta_{ij}-\eta_0\left[1+c_{mn0}k_{pc}\,exp(\,\chi c_{hd,i}\,)\tau_j\right]^{\alpha}\right\}^2 \tag{11}$$

Table 1

Sol viscosity, η_{ij} [mPa·s], depending on time and hydrolysis agent concentration

$c_{hd,i}$[g/g] \ τ_j [s]	0	3 600	7 200	10 800	14 400
0.059	1.2	1.8	2.5	3.2	4.0
0.075	1.2	2.0	2.8	3.5	4.1
0.091	1.2	2.2	3.1	4.0	4.8
0.107	1.2	2.4	3.5	4.7	5.9

Substituting the regressed parameters values in equation (9), the rheokinetic model (12) which describes the performed experiments is obtained:

$$\eta = 1.2\left[1 + 0.78 \cdot 10^{-4}\, exp(13.8c_{hd}\,)\tau\right]^{0.89} \quad [\text{mPa·s}] \tag{12}$$

Experimental data and curves simulated by equation (12) evidence that sol viscosity increases almost linearly in time (Fig. 3) and exponentially with respect to hydrolysis agent concentration (Fig. 4). A good agreement between experimental and simulated data (errors less than 8 %) is observed.

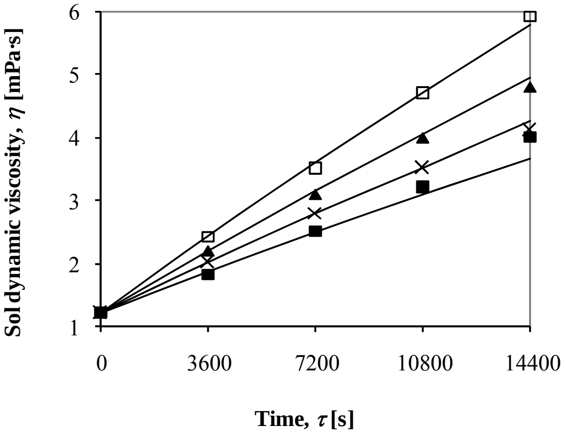


Fig. 3. Sol viscosity versus operating time for various values of hydrolysis agent concentration, c_{hd} (exp: ■ 0.059 g/g, x 0.075 g/g, ▲ 0.091 g/g, □ 0.107 g/g; eq. (12): —)

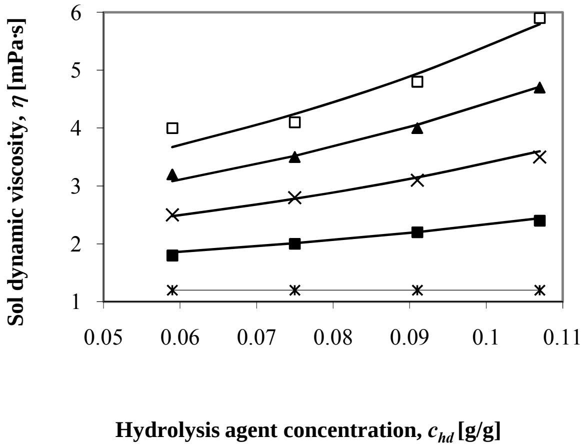


Fig. 4. Sol viscosity versus hydrolysis agent concentration for various values of operating time, τ (exp: * 0 s, ■ 3 600 s, x 7 200 s, ▲ 10 800 s, □ 14 400 s; eq. (12): —)

Values of sol viscosity calculated by equation (12) are illustrated in Fig. 5 which shows in a tridimensional manner an increase of viscosity with hydrolysis agent concentration and operating time.

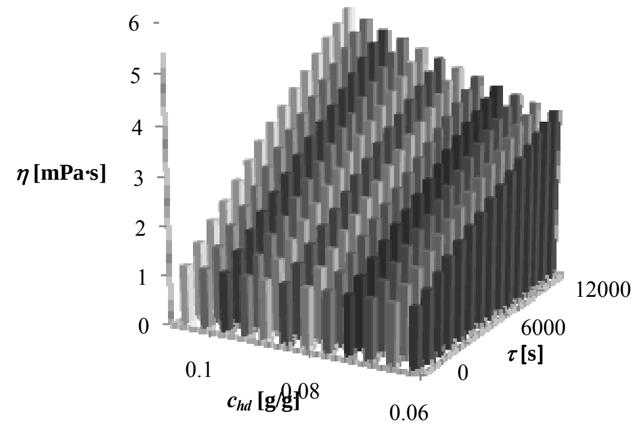


Fig. 5. Sol viscosity, η, versus hydrolysis agent concentration, c_{hd}, and operating time, τ

4. Conclusions

The paper proposed a sol-gel synthesis method of barium titanate starting from barium acetate, titanium isopropoxide, acetic acid, isopropanol and water.

Rheological behaviour of sol formed by precursors mixing was tested at various values of operating time and hydrolysis agent (water) amount. A linear dependency between sol shear stress and shear rate was obtained for water concentrations less 0.107 g/g. Accordingly, the sol could be considered a newtonian fluid with the dynamic viscosity given by the straight line slope.

A rheokinetic model was proposed to determine the sol dynamic viscosity depending on operating time and hydrolysis agent concentration and its parameters were regressed from experimental data.

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