Summary of sol-gel synthesis of materials with electronic applications

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Abstract: *The sol-gel process is a well-known and reliable process for obtaining materials and coatings of different structure and properties. An important feature of this method is the choice of starting precursors to obtain the desired compositions. The complexity of the technology is due to the difficult process control. For this purpose it is necessary to accurately calculate the stoichiometry to obtain the final phase. Thus, the sol-gel technology is widely used as in the production of coatings by immersion and spraying, aerogels and others. However, there are many other applications such as electronic materials that have not yet been well studied. In this study, after a brief explanation of the process, some of the most important applications are considered.*
Keywords: *SOL-GEL, CERAMIC MATERIALS, ELECTRONICS*

1. Introduction

The sol-gel method has been used since 1890 to obtain ceramic materials [1, 2], glass materials [2-4], optical materials [2, 5], superconducting materials [2, 6], enzyme and catalysts carriers [2, 7, 8] and other materials. Currently this technological approach has been successfully applied to produce different products and present a promising rapidly evolving technology [9].The sol-gel technology offers many fundamental advantages compared to the clasical methods, such as use low-temperature synthesizing [10], better homogeneity for multicomponent systems [10], less chemicals consumption [11], insensitivity to the atmosphere [11], durability of properties [11], high yield [12], low equipment costs [9, 13], low production costs [12] and less environmental impacts [11, 14]. The technology provides an opportunity of efectiv control over the physicochemical parameters of the synthesized products by controling kinetic and mechanism of chemical proeses and precision variation of the technological conditions at the different stages of the ongoing reactions in the system [12].

The specific characteristics of sols and gels allow the obtaining of various fibres [15, 10] or thin-film coatings [11], by applying different techniques: spinning or dip-coating [16, 10].

The sol-gel method is based on the use of a homogeneous solution is obtained via dissolving the suitable precursor in a solvent reaction (water or an organic solvent) which is the important stage, no matter if the started precursors is an inorganic salt or various metal alkoxide [2, 17, 18].

There are a number important factors (properties of precursors and reaction conditions) that influence the course of sol-gel processes and determine the characteristics of the obtained final products: metal ion radius, electronegativity, coordination number, reaction medium temperature, reaction time, specificity of the solvent, properties and of the catalyst, concentrations of the catalyst, ratio of water to metal alkoxide and other [2].

The processes that take place in the synthesis of different materials by this method can be divided into several successive technological stages [12]: initially preparation of the solution of suitable precursors, hydrolysis and gradually partial condensation of introduced alkoxides to obtaining a sol, formation of wet gel by a polycondensation process of the hydrolyzed starting precursors, evaporation of the solvent on drying and obtaining xerogel, formation of mechanically stable final products.

The stability of the prepared solution is essential factor and must be kept with constant parameters along a period of time. The processes of hydrolysis and condensation require presence of an acidic or basic catalyst, which influences the hydrolysis and condensation rate and stability of solution [9]. The hydrolysis reaction provoкe formation of sol and then condensation processes lead to the obtain of an specific oxide network – gel [9].

In most cases used raw-materials in the sol-gel technology are those alkoxides, Mx(OR)y, which have composition and structure that are useful in the chemical control of of the properties of synthesised products. It is possible to choose of precursors with apropriate alkyl groups according to the necessary chemical behavior. The application of mixed alkoxides compounds provides an additional opportunity in the efectiv control of the homogeneity and stoichiometry of the final materials [12].

The sol-gel method allow the synthesis of various high-purity porous, monolithic (glasses, ceramic) and bulks materials (oxides, ceramic powders etc.) from different metal alkoxide ($M(OR)_n$ M= Al, Ti, Si, Ta, Hf, Nb, Zr, etc. and R = CH_3, C_2H_5, C_3H_7) [9, 11, 19].

The initial compounds for preparation of a sol are raw materials, which content of a metal or metalloid element surrounded by different ligands. The used metal alkoxides contains various reactive alkoxide groups (–OR), which interact with water in the process of hydrolysis in the presence of a base or a mineral acid as appropriate catalyst. The hydrolysis reaction provoke replace of alkoxide groups with those present hydroxyl groups (–OH), which in the following condensation process form new metaloxane bonds (M–O–M) [11].

When performing research in laboratory conditions, the sol-gel method is widely used to perform experimental syntheses of new materials and develop appropriate technological solutions for obtaining various products [20, 21].

2. Main characteristics of sol-gel technology

Sol-gel is a process of synthesizing a wide range of materials, in particular mixed oxides, which is used due to its advantages of flexibility, low temperature synthesis, etc. The control over the stoichiometry of the obtained product is an advantage of this method [22] The sol-gel method (Fig. 1) is widely used in the synthesis not only of glass and ceramics, but also of organic materials and biomaterials. The process provides a variety of precursors to choose from as starting materials, covering a wide range of systems, including conventional superconductors, high temperature superconductors, ferrites, manganites, multiferroelectrics and other compositions. It offers homogeneous growth of small particles (at nano scale), uniform size distribution and monodisperse nature of the particles. The Zol-gel method is very economical to operate and facilitates and gives predefined stoichiometric compounds.

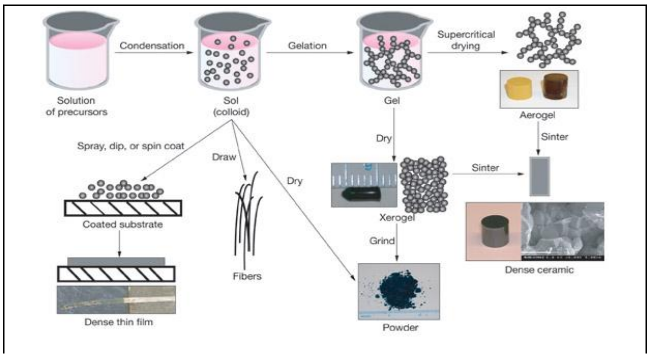

Fig.1 *Presentation of a diagram of the sol-gel method in the work of* Chládová et al.[22].

In this method, the precursors are mixed in solution by hydrolysis and condensation. The reactions combine to form a sol. The sol, or sometimes the precursor solution itself, can be used to prepare gel films by centrifugation, immersion, spraying, or gel fibers. The rapid evaporation of the solvent causes gelling during the actual film or fibrous preparation. The sol may also react with water in an emulsion process and / or be spray-dried to obtain powders, or may undergo additional condensation reactions leading to a gel. Depending on the reaction conditions, the gel may be of a partial or polymeric nature, and it is also possible to make homogeneous and mono-dispersed nanometer or micrometer powders or monolithic gel bodies. The high stress during drying causes many crushing or breaking gels, so dust is formed. Xero gel ("xero" means dry) can be crushed and baked in thick glass and ceramic. It is possible to obtain porous materials in which the solid network of the wet gel is maintained after drying. By using supercritical drying, capillary pressure is avoided and the solvents can be extracted from the gel without cracking. The resulting aerogels have very low densities and may have a solid content of only a few percent by volume. Another way to reduce shrinkage is to remove the hydroxils by modifying the surface and thus reducing condensation. Similarly, the ceramic method is not very useful for the preparation of highly efficient ceramics, as the materials have very large particle sizes, are inhomogeneous and have a high content of impurities [23]. So many studies have focused on various chemical methods for the synthesis of BST powders, e.g., sol-gel, co-precipitation [24-26].

3. Synthesis of materials exhibiting dielectric properties

The investigated ferroceramic materials were obtained by standard sol-gel technology. Phases have been synthesized in $BaTiO_3$ systems - $BaSnO_3$, $BaCeTiO_3$, $BaNdTiO_3$. The modifiers used are in order to increase the value of the relative dielectric constant. Zol-gel processes are carried out according to the above method. The drying processes take place in a different temperature range between 50-100°C. The annealing is carried out in the temperature range 800-900°C. The presented researches are on diagrams from the long experience of the authors over the years for synthesis of ferroelectrics by low-temperature synthesis methods. After obtaining the phases, magnetron sputtering targets are developed and made on different substrates. The team has developed a target in the system $BaTiO_3$ - $BaSnO_3$ whose result of relative dielectric constant is determined in the order of 12000. Table 1 presents a comparative diagram of the experience of other authors on the determination of dielectric constant.

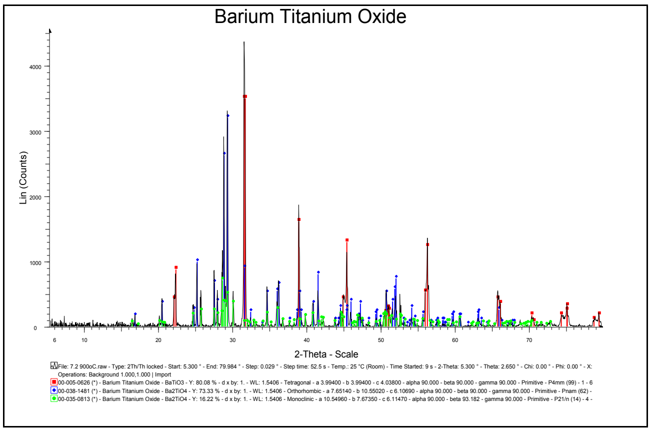

Fig. 1. *XRD of the $BaSnO_3$ via sol-gel synthesis and annealing in 800^OC*

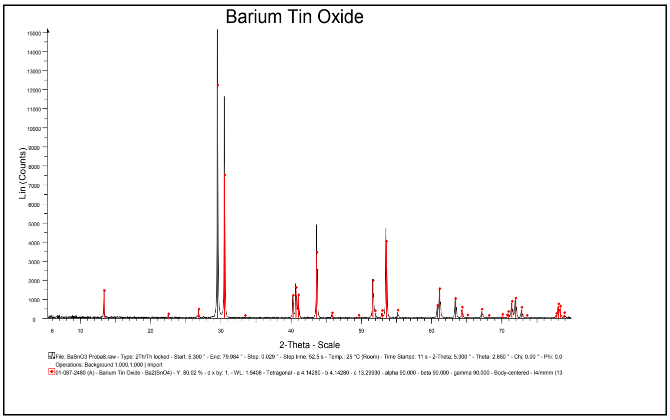

Fig 2. *XRD of the $BaSnO_3$ via sol-gel synthesis and annealing in 700^OC.*

Samuel Fromille and Jonathan developed super dielectric materials, the results of which are cited in Table 1.

Table1. *Influence of layer thicknesses. The data in the first four rows correspond to the discharge of a 528 KOhm resistor, and the last two to a 20 kOhm resistor according to the cited authors. As shown, the thinner the dielectric layer, the higher the capacitance. It is also clear that the lower the "resistor", the higher the capacitance. The difference in the measured dielectric constant probably reflects the unevenness of the handmade structure. [28].*

Test	Dielectric thickness (*d*)	Initial discharge voltage (V_0)	Dielectric constant (ε_R) at operating voltage	Operating voltage	Dielectric constant (ε_R) over entire range
Discharge only (528 kΩ)	1.47 mm	2.20 V	1.81×10^9	0.7 V	8.02×10^8
Discharge only (528 kΩ)	2.46 mm	2.16 V	5.78×10^8	0.8 V	3.52×10^8
Discharge only (528 kΩ)	2.87 mm	1.85 V	4.44×10^8	0.9 V	2.66×10^8
Discharge only (528 kΩ	4.13 mm	2.18 V	4.43×10^8	0.8 V	2.86×10^8
Discharge only (99 kΩ)	2.59 mm	1.43 V	5.0×10^9	0.2 V	1.2×10^9
Discharge only (20.8 kΩ)	0.38 mm	1.60 V	1.27×10^9	0.55 V	
Discharge only (20.8 kΩ)	0.25 mm	1.44 V	1.54×10^9	0.6 V	

Capacitors with two-layer and three-layer structure have some promising advantages for electrical and electronic applications. The three-layer capacitor can to be one of the best options to avoid abrupt change of the electric field from a polycrystalline region to an amorphous region. Comparative electrical parameters of breakdown voltage and electrical conductivity of the three-layer with those of the single-layer amorphous structure, but relatively high dielectric constant also make the three-layer capacitor more attractive to industrial use.

4. Conclusions

Sol-gel method is considered to be very suitable for preparation of high permittivity ferroelectrics due to its advantages to obtain (i) homogeneous ceramic materials, (II) the low temperature of synthesis and sintering, (III) to synthesize materials and compounds with complex structure and phase composition and small grain sizes.

Only recently has attention been paid to the possibility of obtaining electronic ferroelectrics by low-temperature synthesis methods, which would generally exhibit symmetry-breaking instability of the electronic ground state. Another mechanism for electronic ferroelectricity is based on the phenomena of charge arrangement (including charge density waves) in complex oxides. The obtained ceramic materials are aimed for application in electronics and many other industries.

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