NOVEL CHEMICAL SYNTHESIS ROUTES AND PROCESS MODELLING OF NANOSTRUCTURED CERAMIC AND COMPOSITE MATERIALS

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Ceramic nanomaterials have been studied intensively during recent years due to their specific electrical, mechanical or chemical properties resulting from the high interface area/ volume ratio. Many physical, chemical, mechanical or mixed procedures were proposed in the literature to obtain powders, films or bulk nanomaterials. Hydrothermal methods are mentioned to have important advantages such as: one-step environmental friendly process, controlled crystallite size and composition, high homogeneity and sinterability. Nanocrystalline powders from the complex systems Y_2O_3-ZrO_2 PbO-ZrO_2-TiO_2 and BaO-TiO_2 have been obtained by hydrothermal procedures.

Precursor Zr (IV), Ti (IV), Y (III), Ba (II) or Pb (II) aqueous solution mixed in different controlled molar ratios have been used as raw materials. The synthesis pH was adjusted to the desired value using an appropriate mineraliser. Powders have been obtained by hydrothermal treatment of the suspension in a 2L Teflon autoclave (CORTEST, USA) for different times and temperature range. Phase composition of powders was investigated by XR diffraction and RAMAN spectroscopy. Mean crystallite sizes and crystallisation degree were calculated from XRD spectra. The powders microstructure was investigated by SEM method.

A simple general model was proposed for the hydrothermal synthesis of ceramic composite nanopowders. It allows the estimation of powders mean crystallite sizes using the equation

$$r_m \approx (3\, k_B / 4\pi\sigma_0)1/3\ (P_e)1/3\ (-\ln K_{h,g})\text{-}1/3\ [\ln(1/(1-(P_e/S_0))]1/3(1-\alpha)^{1/3} \quad (1)$$

where α is the experimental crystallisation degree, k_B is Boltzmann's constant, $K_{h,g}$ is the hydrolisis constant of the hydrolysis reaction, P_e the concentration of precursor $M(OH)_z$ and S_0 the initial metal concentration.

Extensive studies on the crystallization mechanisms and kinetics of nanocrystalline powders from the systems Y_2O_3-ZrO_2 PbO-ZrO_2-TiO_2 and BaO-TiO_2 have been done to verify the model and optimise the processes.

In the case of hydrothermal synthesis of *zirconia-based nanopowders*, it could be observed that cubic metastable phase is the first formed from the solution due to its lower surface energy compared to the stable monoclinic one (fig. 1).

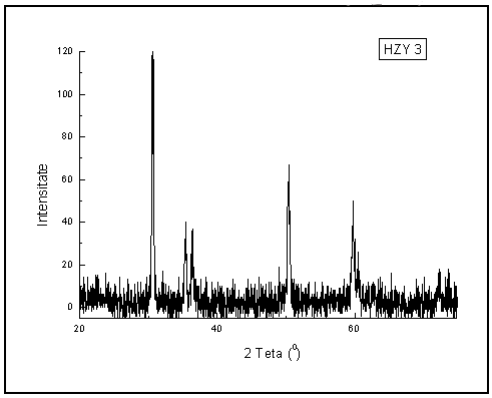

Fig.1. XRD pattern of cubic zirconia powders

Stable monoclinic phase is formed mainly at higher temperatures and long synthesis time. The kinetic of zirconia cubic phase formation was studied assuming the homogeneous nucleation proposed by Avrami in the linear form ***ln(ln 1/1-x)=lnk-nlnt***, where *x* is the crystallisation degree. Activation energy of 12.7 kJmol^{-1} has been calculated corresponding to a diffusion-controlled process [1].

Yttria tetragonal nanopowders with large peaks typically for the nanopowders have been prepared. The calculated mean crystallite sizes were in the range 8 nm to 23 nm [1].

Mean crystallite size (d_{111}) and particle sizes (D_p) were calculated [1]:

$$d_{111} = -7.704 + 0.169\ pH + 0.109\ T\ [nm] \quad (2)$$

$$D_p = 0.6429 + 2.49.10^{-2}\ pH - 1.5797.10^{-3}\ T\ [mm] \quad (3)$$

A model describing the hydrothermal synthesis process of *$BaTiO_3$* powders have been also proposed [1]. The influence of the synthesis parameters (x_1 - working temperature; x_2 - synthesis process duration; x_3 - solution pH; x_4 - molar ratio Ba/Ti in initial solution) on the Ba/Ti molar ratio in the powder (y_1) and crystallisation degree of the synthesis product (y_2) was studied. Process mathematical model is formed by two equations [1]

$$\tilde{y}_1 = \sum_{i=0}^{4} b_i x_i + \sum_{i=j=1}^{4} b_{ij} x_i x_j$$

and

$$\tilde{y}_2 = \sum_{i=0}^{4} a_i x_i + \sum_{i=j=1}^{4} a_{ij} x_i x_j$$

PZT nanocrystalline powders with mean crystallite sizes in the range 4 - 42 nm have been prepared by hydrothermal crystallisation. The Avrami-type equation describes the evolution of crystallite sizes with hydrothermal treatment time [1]:

$$y_i = \ln(\ln 1/1\text{-}r_i) \quad (4)$$

where r_i ratio between d_i and d_{max} and $d_i = \ln(t_i)$.

The calculated values correspond to the experimental calculated crystallisation degree presented in fig 2.

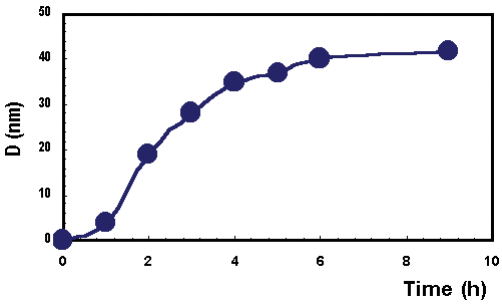

Fig. 2. Mean crystallite sizes of pure PZT powders

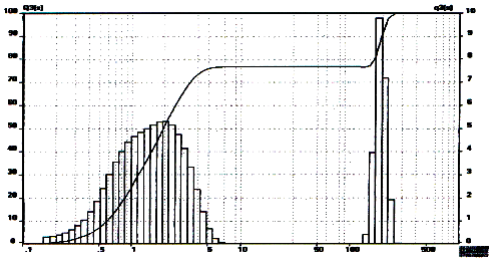

Fig. 3. Granulometric distribution of $Pb(Zr^{0.52}Ti^{0.48})0.975Nb^{0.025}O^3$ powder

Experimental verification of the model proposed for the prediction of mean crystallite size in equilibrium conditions in the systems Y_2O_3-ZrO_2, BaO-TiO_2 and PbO-ZrO_2-TiO_2 shows that model is valid only at low temperatures in the absence of agglomeration processes.

Dense samples (> 95% from theoretical one) have been obtained by uniaxial pressing and sintering the powders synthesised at pH around 5.0 at temperatures over 1300^{0}C. The microstructure of sintered products is presented in fig. 4. These materials were used to study and model the oxygen transport properties in zirconia nanomaterials used for oxygen sensors and solid oxide fuel cells (SOFC) with improved properties at lower working temperatures [2].

Preliminary electrical tests [1] showed that piezoceramic active elements based on PZT obtained by hydrothermal procedures present permitivity values higher than classical PZT ceramics (ε = 400-600) and can be used at higher frequency values. Their TC is higher than for classical PZT ceramics (TC =420^{0}C) and can be used in a large range temperature with a good stability of electro physical parameters for a new generation of sensors, actuators and transducers.

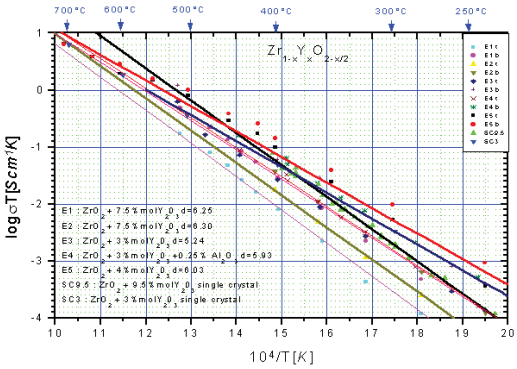

Fig. 4. Conductivity of sintered YTZP

References

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