SYNTHESIS AND CONSOLIDATION OF OXIDE NANOPARTICLES

Igor DANILENKO, Tetyana KONSTANTINOVA, Oksana GORBAN, Galina VOLKOVA, Valentina GLAZUNOVA, Sergei PROKHORENKO, Iryna BRYUKHANOVA

Donetsk Institute for Physics and Engineering NAS of Ukraine, Ukraine, 83114, Donetsk, R.Luxemburg str., 72, matscidep@aim.com

Abstract

In this study we investigate the influence of precursor type, synthesis conditions and dopants concentration on phase composition, particle size and agglomeration degree of different oxide nanopowders, in particular: zirconia, zirconia composites, lanthanum manganite, etc. Also we try to find the influence of characteristics of these powders on consolidation. It was shown that the synthesis conditions have extremely influence on characteristics and structure of different types of oxide nanopowders. In case of zirconia the change of synthesis conditions lead to changing the particle size, agglomeration degree and particle surface properties. Consolidation of nanoparticles under high pressure conditions lead to martensitic phase transformations and this process has extremely depends from synthesis conditions. Zirconia nanopowders which are synthesized from nitrate salts are more stable to phase transition in comparison with powders obtained from chloride salts. For LSM materials we found the strong difference of particles morphology and magnetic properties according to starting material structure. It was found that formation of complex structure of precursor materials during drying and calcinations stage do not allow to obtain the nanoparticles. It was shown that the powders characteristics, what formed during synthesis, are inherited during consolidation process and in ceramics structure and properties.

Keywords: oxide nanopowders, synthesis, powder structure, consolidation.

1. INTRODUCTION

The processes of nanopowders obtaining, properties studies and nanostructured materials utilization lately are very popular in world science, because the properties of these materials promise the substantial change as compared to their conventional analogues [1]. The decreasing of particles size of initial powder from microns to nanosizes allowed not only to improve mechanical properties of ceramic materials but also to find out the change of their physical properties. However the obtaining of nanoparticles with sharp size distribution and the predetermined chemical composition is a complex task in connection with high agglomeration ability of nanoparticles. In most cases we have obtain ceramic powders with dispersion primary particles, which form the firmly linked aggregates are the second particles, which, in same queue, associate in hard or soft agglomerates. The calcinations lead to transform it to polycrystalline particles, with the small value of coherent scattering area and low value of specific surface area. At the same time for fundamental researches except for the requirement of particles connections in the system is very important have the nanoparticles samples with the set of sizes in a nanometric range [1]. There are many methods for the nanopowders obtaining were developed [2-5]. Each of that has own advantages and failings. One of the major disadvantages of most methods is the inheritance of structure of the precursor materials by the structure of the final powder.

In this study we show the influence precursor structures not only on the powder characteristics and properties but on consolidation processes and physical properties of material. In this study we investigate two types of oxide materials: ZrO$_2$-3mol%Y$_2$O$_3$ and lanthanum manganite (La$_{0.7}$Sr$_{0.3}$MnO$_3$).
2. EXPERIMENTAL

Two groups of zirconia nanopowders ZrO$_2$ – 3 mol% Y$_2$O$_3$ (3YTZP) were synthesized by precipitation technique from ZrO(NO$_3$)$_2$·nH$_2$O and ZrOCl$_2$·nH$_2$O salts, type A and type B, consequently. Appropriate amount of Y$_2$O$_3$ was dissolved in nitric acid. The 25% NH$_4$OH was used as a precipitant. After sedimentation the amorphous hydroxide gels are formed. The detailed of this process are published in [5, 6].

In case of lanthanum manganite synthesis the stoichiometric amounts of La$_2$O$_3$, SrCl$_2$·2H$_2$O, Mn(NO$_3$)$_2$·6H$_2$O were used as starting materials and NaOH and Na$_2$CO$_3$ as precipitants for synthesis of La$_{0.7}$Sr$_{0.3}$MnO$_3$ powders. LSM nanopowder obtained by precipitation in Na$_2$CO$_3$ was numbered as NP1 and LSM nanopowder obtained by precipitation in NaOH - as NP2. This numbering was identical to the numbering given in [8], where the measuring of magnetic properties of these powders was made. The detailed of this process are published in [7, 8].

After washing and filtration, the products were dried in microwave furnace with output power 700 W on 2,45 GHz frequency. Drying of hydroxide gel was continued until the termination mass change. The calcination of dried hydroxides or salts were carried out at different temperatures for obtaining desired phase and granulometric composition. The resulting zirconia powders were uniaxially pressed at 50 MPa into rectangular specimens and cold isostatically pressed at different pressures up to 750 MPa. To estimate the properties some of the samples were sintered at 1300 - 1500°C during 2 hours. LSM powders were consolidated by isostatic pressure at 100 MPa and sintered at 1100-1300°C during 2 hours.

The powders obtained after calcination, pressed powders and sintered ceramics materials were characterized by X-ray diffraction employing a Dron-3 diffractometer with CuKα radiation in order to identify the existing phases and determination the crystalline size of powders by the Scherer equation. The fraction of monoclinic ZrO$_2$ was calculated using the equation proposed by Garvie [9]. The fitting and analysis of XRD curves were made by Powder Cell for Windows version 2.4. Powders were also studied by means of TEM (Jem 200 A JEOL). Measurement of mechanical and magnetic properties was carried out in accordance with the appropriate rules.

3. RESULTS AND DISCUSSION

3.1. Zirconia

The main crystal phase of all powder samples synthesized from nitrate and chloride precursors was tetragonal – P4m2 type (cards 17-923, 14-534). The chemical analysis shown the equal amount of Y$_2$O$_3$ – 5,41±0,05 w% for all types of powders. The XRD data were shown that precursor type has not a strong influence nanoparticles size. The average particle size obtained by electron microscopy showed good agreement with the data, obtained by X-ray analysis for all calcining temperatures. The TEM investigation of nanopowders shown that type of precursor has a strong influence on particles agglomeration (Fig.1).

Fig. 1 TEM structure of zirconia powders obtained from ZrO(NO$_3$)$_2$ (a) and from and ZrOCl$_2$ calcined at 1000°C.
Zirconia nanopowders obtained from ZrO(NO$_3$)$_2$ are more agglomerated in comparison with nanopowders obtained from ZrOCl$_2$ at all firing temperatures. At temperatures 400-500$^\circ$C both nanopowders were soft agglomerated. During calcination at temperature 600-800$^\circ$C for type A and 600-900$^\circ$C for type B powders we obtained separated nanoparticles. Agglomeration processes associated with the beginning of sintering between nanoparticles, starting with increasing temperature up to 1000 for type A (Fig. 1a) and absolutely not observed at this temperature and for type B powder (Fig. 1b). Agglomeration associated with the beginning of sintering between nanoparticles at type B powder started at firing temperature 1100$^\circ$C.

The consolidation of these powders under isostatic pressure leads to formation of monoclinic phase (P2c1). The amount of monoclinic phase increase with increasing pressure value. The quantity of transformed monoclinic phase in zirconia nanopowders obtained from ZrOCl$_2$ always bigger than in zirconia nanopowders obtained from ZrO(NO$_3$)$_2$ at equal pressure values (Fig. 2).

The maximum values of monoclinic phase are reached 24% for type A powder and 43% for type B powder after compaction at 750 MPa. The maximum amount of monoclinic phase in the samples treated with the same pressure is reached at different calcination temperatures of powders. There are 800$^\circ$C for type A powder and 900$^\circ$C for type B powder. While the temperature increases to the critical value the agglomeration degree decrease and amount of monoclinic phase increase to maximal value. With further increase of the calcination temperature, when the hard agglomerates are formed, the amount of monoclinic phase is significantly decreased. Changing the type of precursor from ZrO(NO$_3$)$_2$ to ZrOCl$_2$ salts leads to a shift of the temperature of the beginning of the hard agglomerates formation and, consequently, to shift the critical temperature at which the maximum value of the monoclinic phase was observed.

Increasing the quantity of monoclinic phase in the type B powder may be due to the influence of chloride ions on the formation and existence of oxygen vacancies in zirconia. The adsorbed NO$_3^-$ ions at type A powder remove at 200-400$^\circ$C and can not effect on formation and evolution the nanopowder structure and oxygen vacancies during heating. Removing of Cl$^-$ ions from the type B powder is prolonged to 900$^\circ$C. In a powder type B, obtained by calcination at temperatures below 900$^\circ$C, chloride ions can occupy positions on the surface of zirconia particles, and, in accordance with [10], lead to a decrease the stability of the tetragonal phase to external stresses (Fig. 2). Calcinations of nanopowders at 700-900$^\circ$C lead to removing of chloride ions and prevent the integration process between particles at these temperatures.

These differences manifest themselves during sintering. The dependency of density and strength sintered samples obtained from ZrO(NO$_3$)$_2$ versus compaction pressure for all calcination temperatures increase with increasing pressure value. It is the typical behaviour for clean zirconia nanopowders. In case of sintering nanopowders obtained from ZrOCl$_2$ was found a non monotonous dependency density value from pressure value for powders calcination temperatures from 500 to 900$^\circ$C (Fig. 3). We found that then smaller
powder calcination temperature that at the lower pressure reached the maximum values of density and strength of sintered samples. Only nanopowders obtained during calcination at 1000 and 1100°C demonstrate the typical dependency density value from pressure value.

![Image 1](image1.png)

**Fig. 3** The dependence of the density of ceramics sintered from type B powder at 1500°C on the particle size and compaction pressure.

One possible explanation could be - removing chlorine from compacted sample during sintering results in decreasing the samples density especially in samples obtained at high pressures. This behavior is very similar to density evolution what described in [11]. As a result we have a little contradiction: chlorine ions help to obtain separated zirconia nanoparticles, but these nanoparticles are unstable under pressure and inhibit the shrinkage during sintering.

### 3.2. Lanthanum manganite.

In our early study [7, 8] was shown that the magnetization of LSM nanopowder marked as NP2 nanopowder in 3 times less then NP1 nanopowder. The drastic decrease of magnetization is due to the formation a magnetically dead layer at the surface, the thickness of which can even increase as the particle size goes down. Also was shown that drastically difference in the spin-echo signal intensities for NP1 sample and NP2, which does not correlate with the value of the saturation magnetization decreasing (Fig.4).

![Image 2](image2.png)

**Fig. 4** Spin-echo signal intensity vs amplitude of the applied radio frequency field for 50nm and 200nm (NP1), and 20nm (NP2) La_{0.7}Sr_{0.3}MnO_3 nanopowders at 77K and TEM structure of appropriate nanopowders.
These was attributed to the fact that 20 nm NPs are single magnetic domain particles, while the particles which size is 50 nm and larger possess a multi domain magnetic structure. The measuring of spin-echo signal intensity of the samples NP1 and NP2 under identical conditions was shown that curve’s form of NP1 sample is typical for a multi domain ferromagnet (an asymmetric curve with one peak), while the behavior of those for NP2 sample is oscillating and damped. These investigations were shown that the NP2 nanoparticles are monodomains in comparison with typical polydomain NP1 particles.

These changes in magnetic properties of LSM nanopowders we associate with changes in the structure of the powder, which in turn are related to differences in the method of powders obtaining. First of all it should be noted that during obtaining the NP1 powder the Na$_2$CO$_3$ was used as precipitants. During synthesis of NP2 powder the precipitant was NaOH. Change the precipitation agent from Na$_2$CO$_3$ to NaOH lead to formation amorphous structure of sediments instead of crystal structure. The formation of plate like lanthanum carbonate crystals (Fig. 5a) and needle like manganese carbonate agglomerated crystals (Fig. 5b) lead to formation 2 generations of LSM nanoparticles (Fig. 4 up).

**Fig. 5 TEM images of the on a base of La$_2$CO$_3$ – a) and MnCO$_3$ – b).**

During heat treatment the generations of large particles was formed on a base La$_2$CO$_3$ crystals and generation of small particles was formed on a base MnCO$_3$ crystals. Increase the calcining temperature up to 850$^{\circ}$C was conditioned with high stability of lanthanum and manganese carbonates to transformation in oxides. In this case we obtained the typical inheritance the structure of precursors by final powder. Formation of lanthanum manganite particles with wide particle size distribution and relatively large minimal particle size (30-40 nm) helps to multidomain magnetic structur formation. Change the precipitation agent on NaOH lead to formation the amorphous structure of lanthanum and manganese hydroxides (Fig. 6).

**Fig. 6 TEM images of the lanthanum hydroxide - a) and manganese hydroxide - b).**

Heating of these sediments do not lead the formation special structures in comparison with previous case, because the precursors have a homogenous amorphous structure. The crystallization of oxide particles of LSM composition passed at 600-620$^{\circ}$C with formation small (20-30 nm) particles (Fig.4 down) with single modal particles distribution. The absence of large LSM particles in NP2 powder lead to formation
of single magnetic domain particles. It should be noted that the phase composition and total chemical composition for these powders were identical.

LSM sintered ceramics use as porous SOFC cathode material. Samples obtained from singlemodal NP2 nanopowder demonstrate the random porous structure with homogeneous chemical composition. In ceramics samples from bimodal NP1 nanopowder were found the structure and chemical inhomogeneity - a large number of grains rich in manganese (Fig.7).

Fig. 7 SEM images of the sintered LSM samples: from NP2 - a) and NP1 - b) nanopowders.

4. CONCLUSIONS

In this study on two different oxide materials we show that different starting chemicals lead to drastically changing of structure, phase composition and properties of oxide particles. These changes are inherited in properties of consolidated samples during pressing and sintering. Incorrect choose of precursor materials can lead to inability to obtain as separated nanoparticles as the compacts and ceramics with uniform structure.

LITERATURE