NEW METHOD FOR PREPARATION OF NANOMATERIAL POWDERS

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ABSTRACT

This paper deals with relatively new method for preparation of micro and nanomaterial powders. This method is based on replacement of conventional solvents for hydrothermal and solvotermal synthesis of nanomaterials with molten mixture of alkaline hydroxides. This method is efficient and relatively green, because can work with normal atmospheric pressure, with temperatures around 200 °C and without toxic and harmful vapours. This paper will introduce some background of this method and some results realized on our laboratory.

1. INTRODUCTION

Materials with small dimensions like nanomaterials are very important because their properties differ significantly from those of their bulk counterparts. Nanomaterials are widely used in various applications such as photovoltaics, energy cells, biomarkers, sensors, high capacity capacitors, cleaning of environment pollution and in many others.

Nanoparticles and nanocrystals are prepared by many methods, including hydrothermal and solvothermal methods, sol-gel methods, milling, template synthesis, microemulsion processes, physical and chemical vapour processes, chemical bath deposition and many others. Although all these methods have their own advantages, most of them need high vacuum and high temperature or high pressure. Vapour phase processes have limited mass of prepared material, which cause the high price of the products. Also milling processes can produce large quantities of crystal powders, but morphology of the particles is difficult to control. The sol-gel methods are very practical and low cost methods for preparation of nanopowders, but the final products are amorphous and need final calcination at high temperature. Hydrothermal and solvothermal processes are efficient and available for many kinds of nanomaterials. However, in some syntheses are needed capping agents and surfactants, which are not completely removed from surfaces of the final products and can affect some of the properties of the product. In addition, large amounts of organic solvents used in solvothermal processes can bring about environmental pollution. Also sophisticated equipment is required, because of the high pressure is involved in hydrothermal and solvothermal synthesis.

Work in improper melt is other way to preparation of nanoparticles. Are known improper melts of many salts, like nitrates, chlorides and others, but melting points of this melts are on high temperatures above 400 °C. Except these melts exists also improper melts of alkaline hydroxides. Molten alkaline hydroxides are good solvents for many chemical compounds and have relatively low melting points, especially their mixtures and have very low vapour pressures. That makes them very attractive, green and environmentally friendly method for preparation of micro and nanopowders.

2. COMPOSITE HYDROXIDE MELT

The composite hydroxide melt is based on chemical reactions of materials in eutectic hydroxide melts at a temperature of 200 °C and ambient pressure in the absence of organic dispersants or capping reagents. Although the melting points of pure sodium hydroxide, potassium hydroxide and lithium hydroxide are above 300 °C (NaOH 323 °C, KOH 404 °C and LiOH 477 °C), the eutectic points for particular mixtures of these hydroxides, NaOH/KOH 51.5:48.5, LiOH/KOH 31:69 and NaOH/LiOH 71:29 are only about 170 °C, 225 °C and 220 °C, respectively. The mixed hydroxides play the role of the reaction medium. Normally, the synthesis process of the composite hydroxide melt method is a one-step process. All of the raw materials with a certain amount of mixed hydroxides are placed within the Teflon vessel at one time. Then, the nanostructures form within the vessel after heating in a furnace at a temperature around 200 °C for several hours or days. The as-produced materials are crystalline with clean surfaces, which are favourable for further investigating their intrinsic properties. This method is one of the simplest, most versatile, and cost-effective approaches available for obtaining crystalline, chemically pure, single phase powders at lower temperatures and often in overall shorter reaction times with few residual impurities, as compared with conventional high temperature solid-state reactions. The environmental appeal of this method arises from its intrinsic scalability, generality and facility as well as its fundamental basis on the use of hydroxides as the reaction medium.

With this method was in recent years prepared many crystalline powders with wide applicability. From oxides it was for example Bi_2O_3, BaO, ZnO, CeO_2, CuO, Cu_2O, Fe_2O_3, NiO, TiO_2. From mixed oxides that was $BaTiO_3$, $BaMnO_3$, $BaZrO_3$, $SrTiO_3$, Fe_3O_4, $CoFe_2O_4$, $CuAlO_2$, La_2O_3, Nb_2O_5, Co_3O_4 and additionals. With this method can be prepared also sulphides, selenides and tellurides like ZnS, PbS, Bi_2S_3, CdS Cu_2S, PbSe, Ag_2Te, PbTe. Last but not at least can be mentioned applicability of this method for preparation of some hydroxides and many others compounds.

3. PREPARATION OF TITANATES

In this chapter will be described procedure for preparation of titanates, exactly barium titanate $BaTiO_3$ and lead titanate $PbTiO_3$, with this method. Titanates are very important materials with piezoelectric and ferroelectric properties. Titanates find use in high capacity capacitors, detectors, actuators and in many others applications. Commonly are titanates prepared from expensive materials, like titanium alkoxides, by precipitation and subsequent thermal calcination. Base of this method is in use of inexpensive titanium source, like titanium dioxide TiO_2. Procedure for preparation of titanates was subsequent. At first was prepared eutectic hydroxide mixture with 4g NaOH and 5,6g KOH. That mixture was loaded to teflon crucible and let to melt in oven at 200 °C. In next step was 0,16g TiO_2 put into the molten mixture of hydroxides. Mixture was let to dissolve titanium dioxide, reaction (1) and after 30 minutes was added barium sulphate $BaSO_4$ as source of barium ions or lead chloride $PbCl_2$ as source of lead ions. This can be described by reactions (2) and (3). These compounds was chosen, because they have very low hygroscopicity and do not introduce moisture to the the mixture. Barium sulphate was used in stoichiometric amount and lead chloride was used in little excess. After 2 hours in case of $BaTiO_3$ and 6 hours in case of $PbTiO_3$ was reaction terminated. Synthesis of $BaTiO_3$ and $PbTiO_3$ can be described by reactions (4) and (5) respectively. Reaction mixture was then cooled on ambient temperature and dissolved in distilled water. Filtered powder was two times washed with pure distilled water and dried.

$$TiO_2 + 2MOH \rightarrow M_2TiO_3 + H_2O \qquad \{M = Na, K\} \qquad (1)$$

$$BaSO_4 + 2MOH \rightarrow Ba(OH)_2 + M_2SO_4 \qquad (2)$$

$$PbCl_2 + 2MOH \rightarrow Pb(OH)_2 + 2MCl \qquad (3)$$

$$M_2TiO_3 + Ba(OH)_2 \rightarrow BaTiO_3 + 2MOH \qquad (4)$$

$$M_2TiO_3 + Pb(OH)_2 \rightarrow PbTiO_3 + 2MOH \quad (5)$$

Samples of final powders was investigated by scanning electron microscopy, laser confocal microscopy, X-ray diffraction and X-ray fluorescence. From results of this methods was determined, that prepared $BaTiO_3$ is very pure and without traces of remaining TiO_2. That result can be seen on Fig 1. For $PbTiO_3$ was results estimated currently only with X-ray fluorescence and composition is very close to stoichiometric in the range of 3 percents. Other measurements are now in progress.

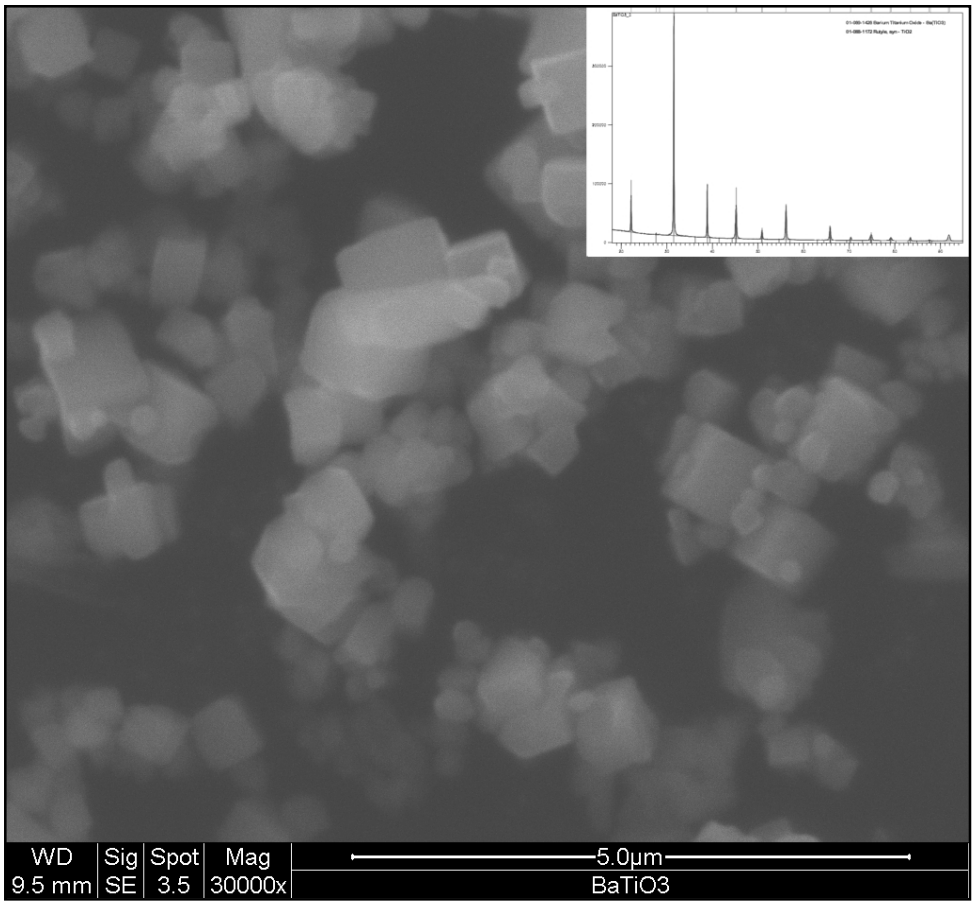

Figure 1 – Crystals of barium titanate prepared in hydroxide melt
On inset is crystal structure from XRD measurement

4. CONCLUSION

In past two years it was prepared on our laboratories on Department of Electric power engineering and Ecology and New Technologies – Research centre on University of West Bohemia many chemical compounds with with this method and new procedures. Exactly that was lead telluride PbTe, lead sulphide PbS, copper(I) sulphide Cu_2S, copper(I) oxide Cu_2O, barium titanate $BaTiO_3$, prepared from new input materials. In accordance with known sources was in first time prepared copper(II) telluride CuTe, copper(II) sulfide CuS and lead titanate $PbTiO_3$. In next chapter will be introduced procedure for preparation of titanates, exactly barium titanate and lead titanate, used in our laboratory. Some results are on Fig. 2.

How can be seen, eutectic hydroxide melt is good approach to preparation of many micro and nanopowders with clear crystaline structure and without any organic compounds. This overcome disadvantages of some others methods, do not need high pressures and offer simple, green and relatively harmless method for preparation of powders with use not only in electrical engineering.

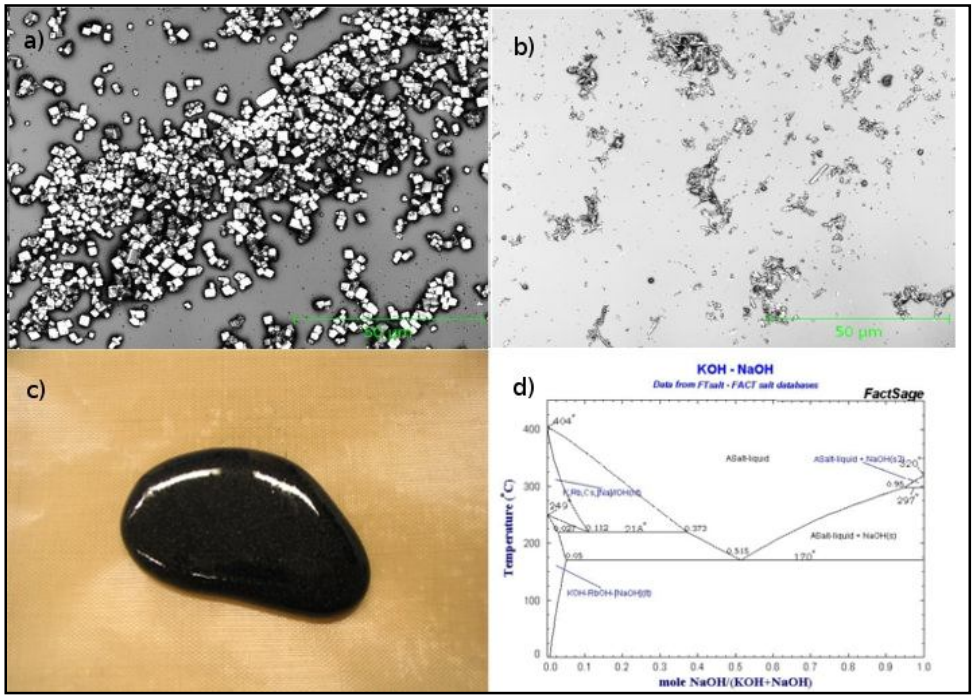

Figure 2 – a) PbTe cubes with laser confocal microscopy, b) CuS rods with laser confical microscopy, d) Black PbS in eutectic hydroxides on Teflon foil, d) Eutectic diagram of NaOH and KOH

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