PREPARATION AND CHARACTERIZATION OF BTO-BFO MULTIFERROIC CERAMICS AS ELECTRICAL CONTROLLABLE FAST PHASE SHIFTING COMPONENT

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Abstract

A rich variety of dielectric, optical, acoustic/piezoelectric, ferromagnetic properties of ferroelectric and multiferroic composite materials open a new perspective for the development of modern accelerators with new type of electron acceleration and control system. A Self-propagating High-temperature Synthesis (SHS) technology for obtaining ceramic materials, based on $(1-x)BiFeO_3–xBaTiO_3$ compositions with various dopant (MgO, MnO, etc.) to get electrically controlled phase tuning and amplitude modulating ultrafast devices has been developed.

The general parameters of the SHS process (temperature and propagation velocity of the combustion front) are measured. The dependences of microstructure (grain size, density, and porosity), as well as electro physical properties of the prepared samples on compaction and sintering thermodynamic variables, such as the pressing pressure and duration, sintering temperature, sintering duration and atmosphere, heating and cooling rates, are experimentally investigated.

INTRODUCTION

Perovskite ferroelectrics and multiferroics are multifunctional materials characterized by a rich variety of properties, such as dielectric, optical, acoustic/piezoelectric, ferromagnetic, etc. These properties may be controlled by external stimuli like electric and/or magnetic fields, temperature and mechanical stress. Nevertheless, multiferroics are the best when it comes to multifunctionality. They combine ferroelectric, ferromagnetic and piezoelectric, etc. properties.

The dielectric permittivity of BSTO and BFO-BTO can be altered very rapidly by an applied bias voltage pulse that make them extremely attractive for high-energy accelerator applications as fast switchers and high-power controlling tuners [1-4].

Since multiferroics combine magnetic and electric properties in the same phase and can present a coupling between the magnetic and electric properties (the induction of a magnetization by an electric field), they provide a new perspective for devices design and can be used to construct new RF phase rotator/shifter (phase and amplitude modulator) based on the simultaneously change of dielectric and magnetic penetration in ferroelectric under the impact of external field [5-7].

$Ba_{1-x}Sr_xTiO_3$ and $(1-x)BiFeO_3–xBaTiO_3$ compositions with MgO and MnO_2 dopant fully satisfy the requirements for a fast electrically-controlled tuner for Brookhaven National Laboratory (BNL) and for high-power fast RF phase shifters to be used for the spallation neutron source (SNS) vector modulation applications. The research and previous calculation of properties of $Ba_{1-x}Sr_xTiO_3$ carried out by A. Kanareykin, E. Nenasheva, et al., show that these materials can be used as key elements of the tunable and switching accelerator components, providing the dielectric constant of the material in the range of 400-500, loss tangent less than $(2-5)\times10^{-3}$ at 10 GHz and the tunability factor (defined as a ratio of the dielectric constant at zero biasing field to that at a specific applied electric field) in the range of 1.15-1.20 at a 5 V/μm (50 kV/cm) biasing field [8]. In this work $[1-y][(1-x)BiFeO_3–xBaTiO_3]-yMn$ solid solutions are suggested which are multiferroic. Both dielectric and magnetic permeabilities of $[1-y][(1-x)BiFeO_3–xBaTiO_3]-yMn$ solid solutions can be controlled by an electric field [9,10]. Till now ferroelectric perovskites were used to solve the aforementioned problems, thus, $[1-y][(1-x)BiFeO_3–xBaTiO_3]-yMn$ multiferroic compositions open new perspective and are the most promising materials for accelerator applications as typical representatives of ferroelectric solid solutions.

In this paper self-propagating high-temperature synthesis (SHS) technologies for obtaining high-quality ceramic materials based on $(1-x)BiFeO_3–xBaTiO_3$ compositions with various dopants (MgO, MnO, etc.) are presented which will be used for getting electrically controlled phase tuning and amplitude modulating ultrafast facilities. These tools can be used in accelerator technologies, particularly at AREAL linear accelerator, which is currently operating at CANDLE Synchrotron Research Institute, for adjusting the 3 GHz wave phase and amplitude used at the accelerating structures [11, 12].

EXPERIMENTS AND PROPERTES INVESTIGATION

The powders of Mn-doped $(1-x)BiFeO_3–xBaTiO_3$ complex oxide have been produced by SHS from powder mixtures of Bismuth oxide, Bi_2O_3, (99.975% purity), Iron oxide, Fe_2O_3, (99.5% purity), Manganese dioxide, MnO_2, (99.9% purity), Barium peroxide, BaO_2, (99.9% purity), Titanium oxide, TiO_2, (99.5% purity), Titanium, Ti, (99.9% purity) and Iron, Fe, (99.9% purity). Materials were synthesized according to the following chemical scheme:

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$$[1-y][(1-x)(1/2Bi_2O_3+(1-K)/2Fe_2O_3+KFe)+$$
$$x(BaO_2+(1-k)TiO_2+kTi)]+yMnO_2+O_2= \quad (1)$$
$$[1-y][(1-x)BiFeO_3-xBaTiO_3]-yMn$$

where k and K are the factors, controlling the exothermicity of the mixture, x and y are the amounts of acceptor dopants, x is taken 0.25, 0.3 and 0.5, y is taken 0.03.

The green mixtures of the desired reactants were prepared by dry mixing in PULVERISETTE 6 Planetary Ball Mill with 200 rpm for 30 minutes. The diameter and height of the pots are 80 mm and 100 mm, respectively.

A portion of metals (Ti or/and Fe) was replaced by its oxide (TiO_2 or/and Fe_2O_3) by changing the values of k or/and K, to control reaction temperature and propagation velocity of the combustion front. The general parameters of the SHS process (temperature and propagation velocity of the combustion front [13]) are measured (Fig. 1). Temperature is measured by C-type (tungsten) or B-type (Pt30%Rh-Pt6%Rh) 0.1 mm diameter thermocouple placed in the centre of the pellets.
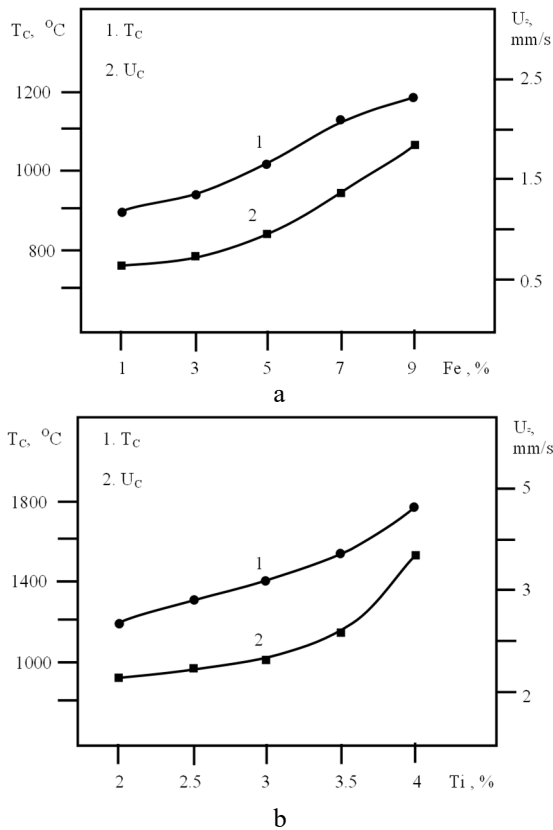

Figure 1: Combustion temperature (Tc) and velocity (Uc) vs. amount of the combustible in the initial mixture: a) Ti is 2%; b) Fe is 2%.

Experiments have shown that the threshold value for k is 0.5 (if K=0) and for K is 0.25 (if k=0). Only at greater values of k and K, the process can proceed under the self-sustaining mode. The greater the value of combustible (k and K), the higher are the combustion temperatures and velocity (Fig. 1). It should also be noted that high combustion velocities provide high output rates of the product from the reactor but undesirable processes of sintering and agglomeration increase (Fig. 2).
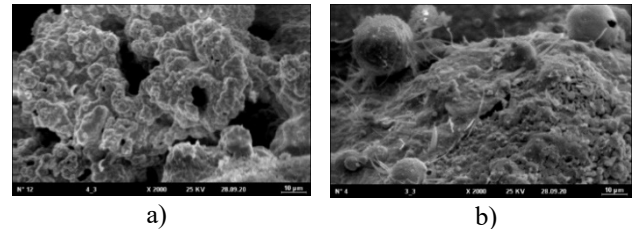

Figure 2: SEM images of $0.3BaTiO_3-0.7BiFe_{0.97}Mn_{0.03}O_3$ composition after SHS. a) K=0.2, k=0.2; b) K=0.3, k=0.6.

The influence of the amount of combustible in the green mixture on the conversion degree of the initial charge to the final product has been investigated. For this, the series of the powder were synthesized at different regimes and characterized by X-ray diffraction (XRD) at room temperature (Siemens D5000), using the CuKa radiation, in the $10° < 2\theta < 130°$ range with 0.01° step size and an acquisition time per step of 10.6 s. And the maximum quantity of a required phase is formed (Fig. 3) when the content of metal powder in the charge is within the limits of 9…11 wt.% (7-9% for Fe, and 2% for Ti).
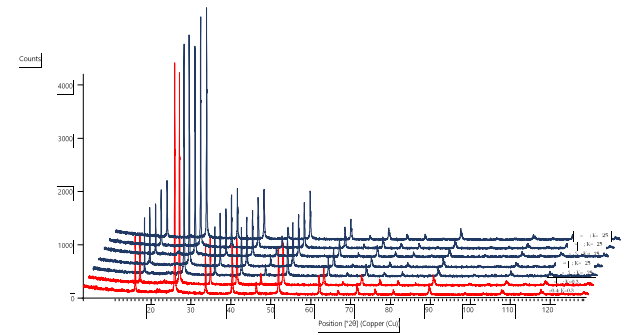

Figure 3: Relative intensity vs. amount of the combustible in the initial mixture for $0.3BaTiO_3 - 0.7BiFe_{0.97}Mn_{0.03}O_3$ composition.

In order to make dense ceramic pellets with desired properties, preparation of powder with the grain sizes about 0.2…5 *um* is required [14]. As a result of calculations and series of experiments, it is found out that the optimal grinding regimes and conditions by PULVERISETTE 6 planetary ball mill are as follows: the relationship of the volume of charge (material to be milled) and milling bodies/balls should be 1/4…1/3; wet ball-milling is faster than dry-milling, but its disadvantage is that the liquid must be removed. Acetone has been used as a milling medium to form a freely flowing cream. Efficient milling is obtained when the volume of acetone is between 100 and 200% of the volume of the charge. The quantity of the grinding body/ball has been taken 70% of the pots volume. The milling body/ball charge contains 4...8 *mm* of sizes (the largest diameter being of the order of a tenth of the diameter of the pot). The rate of rotation (ω_d) of the base disk is 400…600 rev/min. The milling duration is 7 hours.

Synthesized Mn-doped BF–BT powders are pressed into disks of 6…12 mm in diameter and 5...7 mm thick by pressing uniaxially. It is experimentally found out that optimal pressures of pressing to decrease the linear shrinkage factor and increase the density of ceramic samples are about 6000 kg/cm^2.

BF–BT based pellets are sintered between 700 °C and 1000 °C in an electric furnace and air atmosphere under controlled heating/cooling rates of 2.5 °C/min with dwell time of 2 hrs.

The dependence for the linear shrinkage factor and gas-penetrability of samples vs. sintering temperature has indicated that intensive sintering begins with 880 °C (Fig. 4), and the maximum density of the samples is practically obtained at 950 °C (it is important that the main phase is $0.7BiFe_{0.97}Mn_{0.03}O_3–0.3BaTiO_3$).
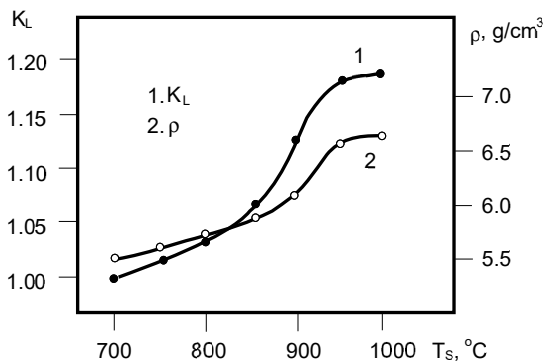

Figure 4: The linear shrinkage factor and density of $0.7BiFe_{0.97}Mn_{0.03}O_3–0.3BaTiO_3$ ceramic samples vs. sintering temperature.

Densification studies were carried out both by direct measurements of the sample density and linear shrinkage after sintering at a specified temperature and by dilatometry. Relative density is measured based on dimensions and weight of the pellets (88…90%, i.e. 5.9…6.1 g/cm^3).

The Au electrodes are deposited by magnetron sputtering for the bias voltage. The dielectric response of the test structures is measured using a HP 4285A LCR-meter and an Agilent N5230 vector network analyzer in the frequency range 0.01-4 GHz. Figure 5 shows the dependences of the tunability factor ($\varepsilon(0)/\varepsilon(E)$ and $\mu(0)/\mu(E)$) versus electric field.
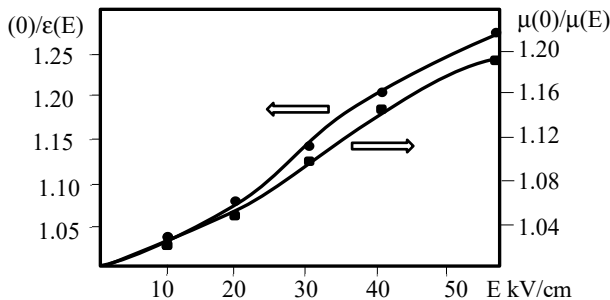

Figure 5: The tunability factors ($\varepsilon(0)/\varepsilon(E)$ and $\mu(0)/\mu(E)$) of $0.7BiFe_{0.97}Mn_{0.03}O_3–0.3BaTiO_3$ ceramic sample vs. biasing field.

SUMMARY AND CONCLUSION

It is established that the threshold value for **k** is 0.5 (if **K**=0) and for **K** is 0.25 (if **k**=0), only at greater values of **k** and **K**, the process can proceed under the self-sustaining mode. Experiments have shown that the temperature (900…1700 °C) and propagation velocity (0.5…4 mm/s) of the combustion front depend on the amount of combustible (Fe and/or Ti have been changed from 3% to 11%), particle size of the initial components (dispersion was 1-5 µm), relative density, as well as the pressure of oxygen and mechanical activation of green mixture. By controlling these critical parameters, powders with the desired/controllable stoichiometry and microstructure are produced. The phase structure investigation shows no other phases when the amount of combustible was about 10% (where Fe-8%, Ti-2%).

As a result of calculations and series of experiments, it is determined that optimal grinding regimes and conditions are as follows: the volume relationship of the charge (material to be milled) and milling bodies/balls should be 1/4…1/3; acetone has to be used as a milling medium to form a freely flowing cream. Efficient milling is obtained when the volume of acetone is between 100 and 200% of the volume of the charge. The quantity of the grinding body/ball has been taken 70% of pots volume. The milling body/ball were of 4...8 mm in size (the largest diameter being of the order of a tenth of the diameter of the pot). The rate of the rotation (ω_d) of the base disk is 400…600 rev/min. The milling duration is 7 hours.

BF–BT based pellets are sintered between 700 °C and 1000 °C in an electric furnace and air atmosphere for 2 hrs under controlled heating/cooling rates of 2.5 °C/min. The dependence for linear shrinkage factor and gas-penetrability of the samples vs. sintering temperature indicates that intensive sintering begins with 880 °C, and the maximum density of the samples is practically obtained at 950 °C.

The tunability factors ($\varepsilon(0)/\varepsilon(E)$ and $\mu(0)/\mu(E)$) for dielectric and magnetic permeability are in the range of 1.22-1.27 and 1.18-1.19 respectively at 60 KV/cm biasing field.

ACKNOWLEDGMENTS

MC6: Beam Instrumentation, Controls, Feedback and Operational Aspects

T24: Timing and Synchronization

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