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Nanostructured $SmFeO_3$ electrophysical properties

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Abstract. Samarium orthoferrite conventional and nanostructured ceramic physical properties and structure investigations are reported in the paper. Ceramic samples have been prepared both by classical sintering method after solid phase synthesis and by Bridgman anvil mechanoactivation after synthesis. The authors have established that the mechanoactivation suppress direct current conductivity and increase spontaneous polarization. Polycrystalline samarium orthoferrite physical properties can be purposefully varied on fabrication stage without doping.

1. Introduction

Samarium orthoferrite ($SmFeO_3$) is representative of multiferroic, it have both ferroelectric and antiferromagnetic properties. From a practical point of view it is a promising material for gas sensors [1] and magnetic field sensors [2]. Ferroelectric and antiferromagnetic subsystems coupling allow one to drive material magnetic properties by electric field and vice versa to drive electric properties by magnetic field [3]. Ceramics and thin films multiferroics promising for memory, functional electronic elements, actuators and MEMS development [3, 4]. Electrical conductivity is the main problem, interfered to multiferroics practical application [3], especially for based on electrotransport properties gas sensors [1]. Authors [5] reports about samarium orthoferrite conductivity increasing with temperature rise, but measurements have been executed only on low temperatures. Gases are most active on high temperatures, thus conductivity dependence in wide temperature range is actual.

As known, main ceramics physical properties directly dependent from temperature-temporal manufacturing regimes, element composition and doping concentration [1, 3, 4]. But doping adding, strengthening some parameters can reduce other useful ceramics characteristics. The aim of presented work is to investigate the alternative ceramic properties control method, based on mechanoactivation. We have thirst studied ceramic samarium orthoferrite electro physics in particular electrotransport properties control possibilities by structure defects concentrations and crystallite sizes changing. Mechanical force action and shift deformation methods have been apply for this aim.

2. Experimental procedure

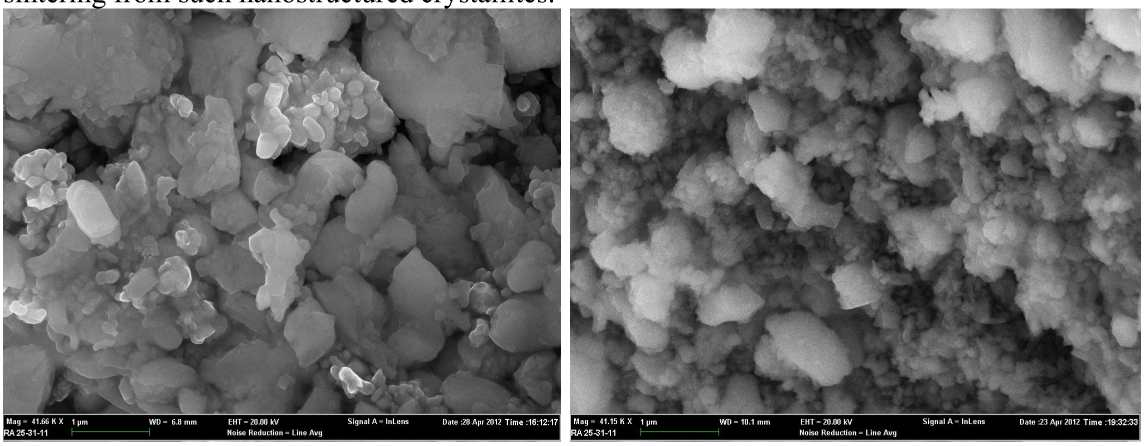
$SmFeO_3$ synthesis have been done from initial chemically pure oxides Sm_2O_3 and Fe_2O_3 in two hours under stabilized temperature T=1200 °C in closed platinum melting pot. The resulting composition phase analysis for impurity phases revealing have been performed on powder X-rays diffractometer HZG-4B in Cu $K\alpha_1,\alpha_2$ radiation, dedicated from common spectra by Ni filter. PCW-2.3 program packet [2a] have been used for Bragg angles corresponding (hkl) diffraction maximums indicating.

Sinthesed samarium orthoferrite mechanoactivation for nanostructuring have been performed by Bridgman anvils, bottom of them have rotated with slow angular velocity. Uniaxial pressure of 200 MPa magnitude has been applied on top anvil. Resulting shift deformation can be evaluate as

$$\zeta = \ln(\nu\, r/d),$$

where ν is the whole anvil rotation angle in radians, equal for used regimes to 12, r and d– sample radius and thickness respectively.

Initial and activated powder samples micrographs have been made by FE-SEM Zeiss SUPRA 25 electron microscope. Activated under 200 MPa pressure sample is characterized by "loose coat" on crystallite surfaces, as clearly visible on SEM-images, presented on Figure 1. Nanostructured powder has increasing crystallites specific surface area and increasing broken bonds ions amount on surface. Activated powder sample crystallite sizes spread has multimodal character and in the range 10-600 nm. Low activation energy values and large diffusion coefficient values is characterized for ceramics sintering from such nanostructured crystallites.



a) b)

Figure 1. SEM-images of samarium orthoferrite powder samples, conventional (a) and mechanoactivated (b)

Disc form ceramic samples from both types of powder, 2 hours sintered on temperature T = 1100 °C have dimensions of 10 mm diameter and ~1 mm thickness. Silver paste has been brazed on 750 °C temperature for two hours on flat surface, formed electrodes. Conventional (etalon) and mechanoactivated ceramics properties have been investigated. Ceramic samples dielectric spectra for a lot of frequencies have been measured in wide positive temperature interval by automated setting, based on immitance measuring device E7-20. For specific dc conductivity measuring has been utilized classical voltmeter – ammeter scheme with 1.5 V batteries as dc power supply using. Ceramic samples spontaneous polarization *Ps* has been studies by classical Sawyer-Tower scheme using.

3. The experimental results and discussion

On X-ray diffraction investigations have been established as well as classical technology manufactured powders and mechanoactivated powders and sintered ceramic samples under room temperature are referring to *Pnma* space symmetry group. Any impurity phases have not been found within the X-ray diffraction analysis sensitivity as presented on Figure 2 diffraction pattern shows. Ceramics unit cell parameters have the following values: a = 5.5935 Å, b = 7.7099 Å, c = 5.3984 Å.

As have been established, powder mechanoactivation results to coherent scattering regions dimensions decreases from 1200 to 50 nm and microstrain $\Delta d/d$ slightly increases. Bragg maximums integral intensities are also increasing after activation as results of crystallite mosaic degree rising [3a]. As known, crystallite mosaic degree rising is followed by crystallites dislocation concentration increasing. Thus, after 200 MPa mechanoactivation dislocations concentration prevails on point defects concentration in $SmFeO_3$ powder generated structure defects. Polycrystalline point defects concentration can be estimated qualitatively only from X-ray diffraction profiles broadening and integrated intensities changing. A significant diffraction profiles broadening activated under 200 MPa pressure samarium orthoferrite have not been found. But, it should be understood, that Bridgman anvils powder mechanoactivation on lot of pressure can cause to dynamic recrystallization processes developing, accompanied by coherent scattering regions increasing and some microdeformations decreasing. The absorption of some crystallites to other is often took place in such situations [4a], but we have not study this phenomenon.

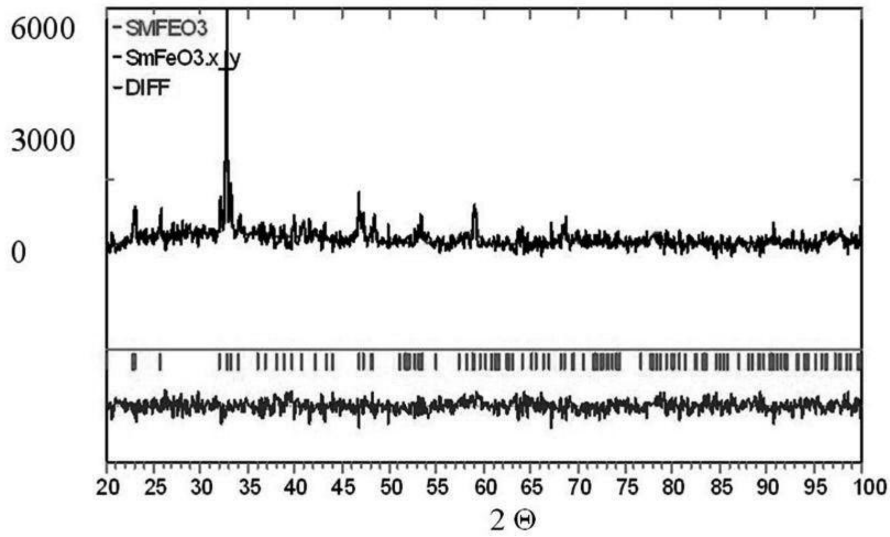


Figure 2. Samarium orthoferrite diffraction pattern

The dielectric constant ε, as ferroelectric fundamental properties, has been investigated in temperature range. The results for a number of frequencies are presented on Figure 3. As can be seen unactivated $SmFeO_3$ temperature dependences (a) are not corresponded to relaxor ferroelectrics. This is because that conventional sample has a sufficient amount of impurities, with energy, corresponded to located in the forbidden zone energy levels. During sample heating an impurity levels thermal devastation impurity levels and charge carriers transport in the conduction band took place. Enough large through conductivity of the sample masks its ferroelectric properties and it is not always possible to refer rare earth orthoferrites to relaxor ferroelectrics. This is confirmed by ceramic specific conductivity temperature dependence plots, presented on Figure 4. As have been found the activated sample specific conductivity in wide temperature range is two orders of magnitude less than that of the etalon sample.

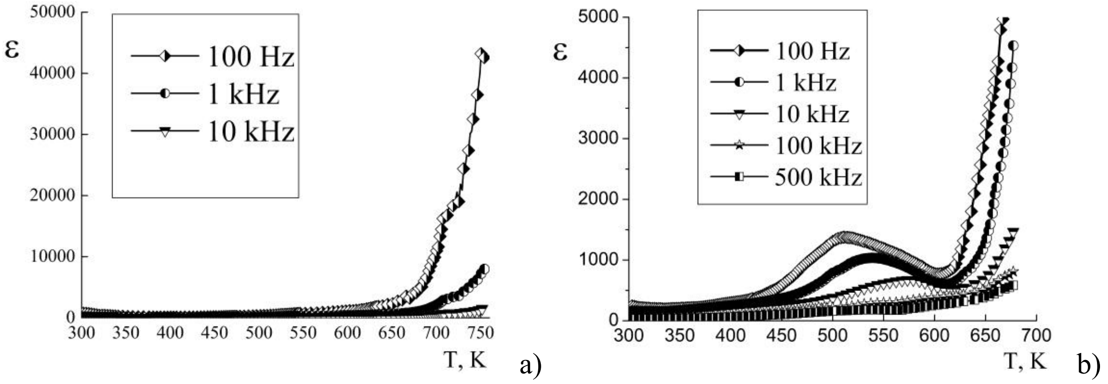


Figure 3. $SmFeO_3$ ceramic permittivity temperature dependence for a number of frequencies: a) etalon sample, b) mechanoactivated sample.

Mechanoactivation reduces the activation energy of impurities diffusion processes under ceramics sintering and facilitate their exit to the surface. Activated sample permittivity ε temperature and frequency dependence, presented on Figure 3 (b) has relaxor character. Temperature of permittivity maximum is offset to right and maximum value is decreased as measuring field frequency rise.

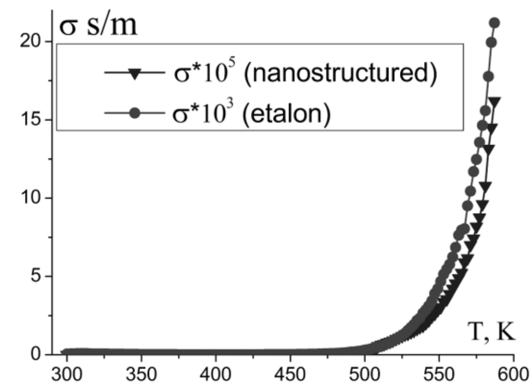


Figure 4. $SmFeO_3$ ceramic specific conductivity temperature dependence for conventional and mechanoactivated samples.

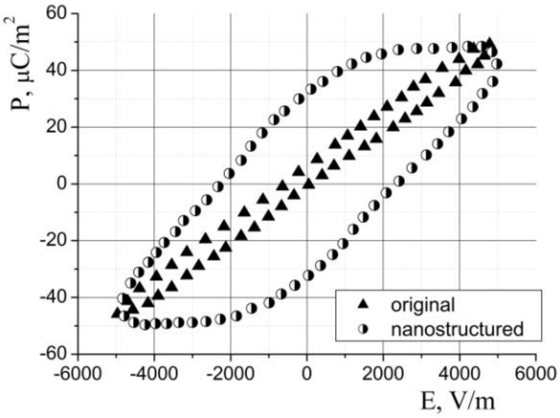


Figure 5. $SmFeO_3$ ceramic hysteresis loop for etalon and mechanoactivated samples.

The possibility of spontaneous polarization *P* switching by electric field or by mechanical pressure is the main ferroelectric property. Spontaneous polarization *P* hysteresis loops as a function of applied electric field *E*, are presented on Figure 5. For unactivated $SmFeO_3$ has a weak and distorted loop, characteristic for defective crystals-antiferroelectric, ferroelectric properties are mild. $SmFeO_3$ mechanoactivation lead to spontaneous polarization *P* rising and hysteresis loop saturating, loop becomes similar to loop of barium titanate, as a classical ferroelectric.

4. Conclusions

The authors have proposed technical solution for purposeful control physical properties on fabrication stage. Both conventional and mechanoactivated $SmFeO_3$ samples structure and dielectric properties are investigated, presented diagrams proves ferroelectric properties. Electrical conductivity is rather stable in wide positive temperature range. It have been demonstrate, that samarium orthoferrite mechanoactivated sample electro physical characteristic is sufficient higher, than etalon sample. Dosed pressure nanostructured mechanoactivation after synthesis is universal modifications method for any complex material without alloying element adding.

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