Solid State Sciences 59 (2016) 1–6

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

Synthesis and structural properties of (Y, Sr)(Ti, Fe, Nb)$O_{3-\delta}$ perovskite nanoparticles fabricated by modified polymer precursor method

T. Miruszewski*, P. Gdaniec, J. Karczewski, B. Bochentyn, K. Szaniawska, P. Kupracz, M. Prześniak-Welenc, B. Kusz

Department of Solid State Physics, Faculty of Applied Physics and Mathematics, Gdansk University of Technology, Narutowicza 11/12, 80-233, Gdansk, Poland

ARTICLE INFO

Article history:
Received 13 May 2016
Accepted 28 June 2016
Available online 29 June 2016

Keywords:
Doped $SrTiO_3$
Perovskite
Wet-chemical synthesis
Nanoparticles

ABSTRACT

The yttrium, iron and niobium doped-$SrTiO_3$ powders have been successfully fabricated by a modified low−temperature synthesis method from a polymer complex. The usage of strontium hydroxide precursor instead of conventional strontium nitrate or strontium carbonate provides to the possibility of significant decrease of annealing temperature. It allows to prepare a material with sphere-shape grains of nanometric size (15−70 nm). The results of thermal analysis indicate that the crystallization of precursor takes place at different stages. The product after heat treatment at 600 °C for 3 h in air was also characterized by X-Ray diffraction method (XRD) and Fourier transform − infrared spectroscopy (FT-IR). After the crystallization and the impurity removal process, a single-phase material was obtained in case of all analyzed samples. The morphology of obtained nano-powders was also studied by a scanning electron microscopy (SEM). It can be concluded, that this method allows obtaining a perovskite phase of a metal doped $SrTiO_3$ with nanometric particles.

1. Introduction

The strontium titanate $SrTiO_{3-\delta}$ (STO) is an advanced ceramic material showing a phase transition at temperature 105 K. At lower temperatures it transforms to the tetragonal antiferrodistortive (AFD) structure [1]. This material exhibits a very wide variety of application in electronic devices like memristors, grain boundary barrier-layer capacitors [2], oxygen gas sensors [3], solar cells [4], solid oxide electronic devices [5–7] or it can be a candidate for efficient photocatalysts [8]. It was previously shown that electrical and structural properties of perovskite-type oxide structures strongly depend on a fabrication method [9]. For many applications the microcrystalline doped strontium titanate is prepared by the conventional solid-state reaction (SSR) method. However, this method needs a high sintering temperature, which causes the growth of grains of the obtained material. The high temperature also causes a series of disadvantages from an economical point of view. On the other hand, wet-chemical methods, like a sol-gel, self-combustion method, Pechini or hydroxide method have been proved to be more suitable for the preparation of nanocrystalline $SrTiO_3$ particles [10,15,16].

In recent years, the nanoceramics have become very important and promising materials of applied research. The tremendous interest in the last years is caused due to their significance for the important applications as advanced materials in novel devices [10]. Among them, metal-oxide nanoparticles have considerable attention. Some interesting quantum confinement effects, the large number of intrinsic surface states and surface defect centers affect the attractive physical and electrochemical properties. In polycrystalline ceramics the amount of grain boundaries significantly increases with a decrease of grains size. The grain boundaries and the surface defects are significantly responsible for oxygen diffusion what is an important factor in materials for Solid Oxide Fuel Cells and gas detectors [11–14].

In this work, according to the previous reports about the wet chemical synthesis of pure strontium titanate [16], the authors present the modified synthesis method allows to obtain the nanometric powder of Y, Fe and Nb-doped $SrTiO_3$ at a low calcination temperature. It is important to underline that in contrast to the pure $SrTiO_3$ material, only a few papers about this particular synthesis method and containing thorough analysis of properties of donor and/or acceptor doped strontium titanate nanoparticles

* Corresponding author.
E-mail address: tmiruszewski@mif.pg.gda.pl (T. Miruszewski).

http://dx.doi.org/10.1016/j.solidstatesciences.2016.06.011
1293-2558/

were reported, *i.a.* [15,16]. The Y, Fe and Nb dopants were selected according to previous investigations of our group as well as in reference to the certain literature report [6,17,18]. This choice of dopants will confirm the possibility of applying the presented method of synthesis in the case of doping each sub-lattice of perovskite structure individually as well as simultaneously doping both of them. The obtained products were characterized from a structural point of view.

2. Experimental procedures

The studied powders: $Y_{0.07}Sr_{0.93}TiO_{3-\delta}$, $Y_{0.07}Sr_{0.93}Ti_{0.8}Fe_{0.2}O_{3-\delta}$ and $SrTi_{0.98}Nb_{0.02}O_{3-\delta}$ were prepared by a modified wet chemical synthesis, called as "mud synthesis" (MS) in this paper, from the following precursors: $Y(NO_3)_3 \cdot 6H_2O$, $Sr(OH)_2 \cdot 8H_2O$, $Ti(OCH_2CH_2CH_2CH_3)_4$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Nb(OCH_2CH_3)_5$. Nominal notations and abbreviations of the samples are listed in the Table 1.

At the initial state, the strontium precursor – $Sr(OH)_2 \cdot 8H_2O$ – was grinded in an agate mortar for 30 min. Then, an absolute ethanol was added to the powder and hand-mixed in mortar for 30 min. The amount of absolute alcohol was chosen to obtain slurry, according to the organoleptic observations. After that, the metal-organic precursors of Y/Fe/Nb in the appropriate molar ratios were added to the mixture. Finally, the Ti-precursor was added to the mixtures. It is important to notice here, that in all samples the 20 % excess amount of strontium precursor was added. According to previous literature report, it is necessary to obtain a stoichiometric composition of the final product. An eventual Sr excess which will not take a part in the $SrTiO_3$ phase formation, should be visible in a form of a $SrCO_3$ impurity, as it was shown in Zhu et al. work [16]. Subsequently, the mixture was vigorously stirred and ground for 30 min until it reached a homogenous slurry form. The preliminary green powder was obtained after drying in air at 80 °C for 24 h and grinding again to the powder form. After that, the precursor was calcined at different temperatures (200–600 °C) for 3 h. The furnace was preheated to the desired temperature before the powder was inserted. In this synthesis process, a very fast kinetic of powder heating is necessary. At this stage of the powder preparation, the strontium carbonate impurity $SrCO_3$ had to be removed. Therefore, the 3 M acetic acid was added to the powder and it was left in ultrasonic bath for 1 h. The obtained slurry was filtered with distilled water and ethanol for 15–20 times with Büchner funnel. At the final stage, the powder was dried in air at 80 °C for approximately 4 h until all water/ethanol is removed. In order to summarize the procedure of the synthesis, it is shown in the flow chart in Fig. 1.

The phase composition of an obtained powder was examined at room temperature by the X-Ray diffraction method (XRD) using the Phillips X-Pert Pro MPD diffractometer with $Cu_{K\alpha}$ (1.542 Å) radiation. The patterns were analyzed by the Rietveld method using the PANalytical High Score Plus software with the pseudo-Voigt profile function applied. Moreover, in order to check the temperature influence of the phase composition, the high-temperature XRD measurements were performed in 200–600 °C range in air. The average size of crystallites d_{XRD} was estimated using the Scherrer's formula. The morphology and average particle size d_{SEM} of the powders were observed by the FEI Quanta FEG 250 Scanning Electron Microscope (SEM) operating with a secondary electron detector in a high vacuum mode with the accelerating voltage 10 kV. Simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed under synthetic air condition with heating rate 15 °C/min from 40 °C to 700 °C using Netzsch STA 449 F1. In order to account for buoyancy effects, a correction curve with an empty alumina crucible was first obtained and then subtracted from the experimental results. The FT-IR spectra were measured at an ambient temperature using Perkin-Elmer spectrometer with the Frontier FTIR MIR/FIR model. The obtained spectra of the samples pressed into KBr pellets were recorded in the wave number range 400–4000 cm^{-1} using the KBr beam splitter.

Table 1
Nominal notations and abbreviations of doped strontium titanate powders.

Nominal composition	Used abbreviation
$SrTi_{0.98}Nb_{0.02}O_{3-\delta}$	STNbO
$Y_{0.07}Sr_{0.93}TiO_{3-\delta}$	YSTO
$Y_{0.07}Sr_{0.93}Ti_{0.8}Fe_{0.2}O_{3-\delta}$	YSTFO

3. Results and discussion

In order to determine the crystallization of a perovskite phase from the precursor, the XRD measurements were performed as a function of temperature. Fig. 2 presents the main $SrTiO_3$ reflection (~32.2°) measured at different temperatures for YSTO (Fig. 2a), YSTFO (Fig. 2b) and STNbO (Fig. 2c) samples.

In all samples, this peak can be indexed as the main $SrTiO_3$ reflection. In YSTO and STNbO powders the partial crystallization occurs at very low temperature equal to 80 °C. In these samples a gradual increase of intensity is observed. It indicates that the products have higher crystallinity and larger crystallite sizes when the annealing temperature is increasing. In this case a perovskite phase formation is observed at lower temperature compared to reports of Zhu et al. [16], wherein they observed an immediate increasing of intensity in pure $SrTiO_3$ sample above 300 °C. The results presented in Fig. 2 showed, that in contrast to YSTO and STNbO, in YSTFO sample the main reflection can be recorded only above the 450 °C. The difference between YSTO/STNbO and YSTFO XRD spectra may be caused by different chemical composition (additional dopant in Ti-site) and different thermodynamic properties of samples. In YSTFO, the energy which is needed to initiate the exothermic crystallization process may be probably much higher. Thus the crystallization rate of polymer precursor breaking down into strontium titanate may be higher. Concluding, the HT-XRD results showed that it is possible to obtain a single phase material even at a very low temperature of calcination (80 °C for YSTO or STNbO and 500 °C for YSTFO).

The average size of crystallites of studied powders was also calculated from the Scherrer's formula and presented in Fig. 3.

For all samples, the estimated crystalline sizes are similar but only at higher temperatures. They increase from ~35 nm at 200 °C to ~65 nm at 600 °C. The almost linear increase of d_{XRD} value was noticed for studied STNbO and probably for YSTFO powders. For the YSTO sample, the behavior seems to be not linear. However, authors claim that almost the same kinetic of the crystal growth for all samples was noticed. Concluding, it can be stated, that the final size of crystallites of doped strontium titanate powders can be controlled by the calcination temperature.

In order to find the mechanism of thermal behavior of studied precursor, the simultaneous thermogravimetric analysis (TGA) with differential scanning calorimetry (DSC) has been performed. The DSC and first derivative of mass (dm/dT) (DTGA) curves of non-calcined precursor are shown in Fig. 4.

The spectra show two characteristic regimes in all curves. In the first, between 50 °C and 250 °C, an endothermic peak can be found in results of all powders. The corresponding peak is also visible in dm/dT signal what indicates the high mass loss in this region. It is possible that this peak can be attributed to the volatilization of adsorbed ethanol and water in initial precursor. In the second stage,