Features of reactive SPS of SrTiO$_3$–TiO$_2$ biphasic ceramics

A P Zavjalov$^{1,2}$, O O Shichalin$^{1,3}$, S A Tikhonov$^{1,4}$ and D Yu Kosyanov$^1$

$^1$Far Eastern Federal University, 10 Ajax Bay, Russky Island, Vladivostok 690922, Russian Federation
$^2$Laboratory of Methods of Synchrotron Radiation, Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, 18 Kutateladze Street, Novosibirsk 630128, Russian Federation
$^3$Institute of Chemistry, Far-Eastern Branch of the Russian Academy of Sciences, 159 100-let Vladivostoku Avenue, Vladivostok 690022, Russian Federation
$^4$Kamchatka Branch of the Geophysical Survey of the Russian Academy of Sciences, 9 Piip Boulevard, Petropavlovsk-Kamchatsky, 683023, Russian Federation

E-mail: Zav_Alexey@list.ru

Abstract. SrTiO$_3$ and biphasic SrTiO$_3$–TiO$_2$ ceramics were obtained by reactive spark plasma sintering (SPS) of mixtures of strontium carbonate SrCO$_3$ and titanium dioxide TiO$_2$. For monophasic SrTiO$_3$, there is a linear seal of the mixture in the heating process. Biphasic ceramics at a temperature of about 1320°C are characterized by eutectic melting of the SrTiO$_3$–TiO$_2$ mixture, which allowed estimating the temperature gradient in the system $\sim$77$^\circ$/sm. Microstructural studies have confirmed the formation of biphasic SrTiO$_3$–TiO$_2$ ceramics with a homogeneous structure and a grain size of 1÷2 $\mu$m.

1. Introduction

A significant share of the electricity received by mankind is limited by the performance of heat engines, which leads to energy losses in the form of dissipated heat. The efficiency of power plants can be increased by directly consuming waste heat, for example, for heating. However, it is important to be able to get additional electricity. Direct conversion of heat to electricity is possible using thermoelectric materials, which are used, for example, in systems with radioisotope thermoelectric generators to ensure autonomous operation of satellites, beacons, etc.

The key characteristic of these materials is the thermoelectric q-factor $ZT$. At relatively low temperatures (up to 300$^\circ$C), the $ZT \sim 1$ value is typical for widely used materials based on Si–Ge and Bi–Sb–Te [1, 2]. At temperatures of 500–1000$^\circ$C, high $ZT$ values (up to ~1.5) are achieved using compounds with heavy metals [2], but at higher temperatures ($\geq$1000$^\circ$C), these materials may be subject to thermal degradation. Therefore, more stable oxide compounds should be considered for use as high-temperature thermoelectrics.

Due to the features of the state density function, low-dimensional electronic systems have high thermoelectric characteristics [3]. Based on data for thin Sr layers Sr(Ti$_{0.8}$Nb$_{0.2}$)O$_3$ in the amount of SrTiO$_3$ [4] and other reported parameter values, the paper [5], using numerical modeling, showed that the structure consisting of cubic grains (Sr$_{1-x}$La$_x$)TiO$_3$, 16 unit cells in size, separated by Sr(Ti$_{0.8}$Nb$_{0.2}$)O$_3$ layers in 1 unit cell, could reach $ZT$ values $\sim$1.15–1.2 at room temperature. This is achieved due to the properties of 2D electron gas (2DEG) in thin layers, as well as their influence on
the transport properties of the entire material. Creating such a structure requires the use of complex nanoconstruction techniques. In [6], cubic particles of this composition were obtained, but they have a much larger size, and it is not clear how to consolidate them without destroying the thin layers.

However, [4] demonstrated the spontaneous occurrence of 2DEG at the interface between the SrTiO$_3$ and TiO$_2$ layers. Therefore, in the review [7], the authors proposed a biphasic SrTiO$_3$–TiO$_2$ ceramics with a staggered grain structure of the components. The phase interleaving must form a connected 2DEG network that permeates the entire material. A similar structure of dense ceramic grains was obtained earlier for the Y$_2$O$_3$–MgO system using the SPS method [8]. This paper presents the features of obtaining biphasic SrTiO$_3$–TiO$_2$ ceramics (50:50 for vol.%) by reactive SPS of a powder mixture of SrCO$_3$ and TiO$_2$, as well as monophasic SrTiO$_3$ ceramics for comparison from a powder mixture of the same components (1:1 by mole).

2. Experimental section

Commercial powders (Sigma-Aldrich) of titanium dioxide TiO$_2$ (anatase, 99.8%) and strontium carbonate SrCO$_3$ (99.9%) were used to prepare two types of mixtures. The first type is designed to produce SrTiO$_3$ ceramics by the reaction SrCO$_3$ + TiO$_2$ → SrTiO$_3$ + CO$_2$↑. The second type has an excess of TiO$_2$ to produce biphasic SrTiO$_3$–TiO$_2$ ceramics (50:50 for vol.%) taking into account the phase transformation anatase→rutile during SPS. The mixtures were prepared by grinding in a Pulverisette 6 planetary mill (Fritsch, Germany) in an isopropanol at 280 rpm for 10 hours, followed by drying, granulation, and calcination steps to remove organic components. Reactive SPS experiments were performed on the SPS-5155 (Dr. Sinter Lab, Japan) in a graphite crucible Ø15 mm (sample 2 g) in a vacuum (~6 Pa) at a mechanical load of ~21.5 MPa and isothermal exposure at 1000–1400°C for 5 min.

The microstructure and elemental analysis of the samples were analyzed by the scanning electron microscope (SEM) Carl Zeiss Ultra 55+ (Carl Zeiss, Germany) with an energy-dispersive X-ray (EDX) detector X-Max (Oxford Instruments, UK). The phase composition was performed using a powder X-ray diffractometer D8 Advance (Bruker, Germany) using CuK$_{α1,2}$ doublets and a range of double reflection angles from 5° to 90° with a step of 0.02° and a speed of 0.5°/min.

3. Results and Discussion

Figure 1 shows the densification curves and the temperature modes of the obtained ceramic samples. Attention should be paid to the stage of linear densification of SrTiO$_3$ ceramics (Figure 1a) (in the first ~10 minutes of the experiment), which is not observed when obtaining biphasic SrTiO$_3$–TiO$_2$ ceramics (Figure 1b). This difference can be explained by the higher concentration of SrCO$_3$ in the mixture for the preparation of monophasic SrTiO$_3$ ceramics since strontium carbonate is much softer than titanium dioxide. That is, when sintering monophasic ceramics, due to the deformation of the SrCO$_3$ phase, the mixture is compacted as it is heated. For biphasic SrTiO$_3$–TiO$_2$ ceramics, the TiO$_2$ phase forms a stronger frame and does not allow such deformation.

In addition, for both mixtures, it can be noted that exposure at 1000°C does not lead to significant densification. At higher temperatures, the nature of the seal changes significantly; however, significant densification occurs at temperatures from 1000°C to 1100–1200°C and changes slightly at higher temperatures. According to XRD data, the SrCO$_3$ phase is not detected for samples sintered at 1000°C, i.e., the reaction between the components occurs at lower temperatures. Therefore, it can be concluded that non-reactive sintering processes are activated in the temperature range from 1000°C to 1100–1200°C.

For biphasic SrTiO$_3$–TiO$_2$ ceramics, it was not possible to sinter the mixture at 1400°C, because when the temperature reached ~1320°C, a sharp increase in densification occurred, and the experiment was interrupted. This sintering behavior is usually observed when the material is melted. In this case, the authors associate melting with the fact that there is a eutectic for the SrTiO$_3$–TiO$_2$ system. Sintering at 1300°C was carried out to the end. However, the resulting sample had a hole in the central part. In addition, a small jump in densification in the ~15th minute of the experiment can be observed.
This result is associated with the heterogeneity in the temperature distribution in the sintered sample. There was a slight overheating in the central region, which led to local destruction of the melting region and was reflected in a jump in densification, after which sintering continued in normal mode. Sintering with exposure at 1200°C did not have the characteristic features of melting. Therefore, this mixture was sintered separately at an intermediate holding temperature of 1250°C, which also had no special features. The melting of the sample at a temperature of ~1320°C and the destruction of the central region at ~1260°C in the experiment with exposure at 1300°C makes it possible to obtain unique information about the SPS process – to estimate the temperature gradient ΔT/Δr ~ 77°C/sm.

Figure 1. Densification curves and temperature modes for ceramics obtained by reactive SPS of powder mixtures of strontium carbonate SrCO\(_3\) and titanium dioxide TiO\(_2\): (a) SrTiO\(_3\); (b) SrTiO\(_3\)–TiO\(_2\) (50:50 for vol.%).

Figure 2 shows X-ray diffractograms of ceramic samples obtained at 1200°C for monophasic and 1250°C for biphasic ceramics. The complete reaction can be seen with the formation of the target phases – taulsonite SrTiO\(_3\) (lattice constant 3.90481 Å for monophasic and 3.90778 Å for biphasic ceramics) and rutile TiO\(_2\) (lattice constants \(a = b = 4.59492\) Å and \(c = 2.96147\) Å for biphasic ceramics). No impurity phases were detected. Figure 3 shows the microstructure and elemental analysis data (at.%) of these ceramics. The formation of a homogeneous microstructure with an average grain size of 1÷2 µm is shown. Elemental composition based on the results of EDX studies using the XRD data. Using the EDX method, which provides information averaged over a volume larger than the phase sizes, allowed for local phase identification. In Figure 3b, dark grains correspond to the composition of TiO\(_2\), and light grains correspond to SrTiO\(_3\). No impurity elements were detected.

Figure 2. X-ray diffractograms for ceramics obtained by reactive SPS of powder mixtures SrCO\(_3\)–TiO\(_2\): (a) SrTiO\(_3\); (b) SrTiO\(_3\)–TiO\(_2\) (50:50 for vol.%).
Figure 3. SEM images of the ceramics obtained by reactive SPS of powder mixtures SrCO$_3$−TiO$_2$: (a) SrTiO$_3$; (b) SrTiO$_3$−TiO$_2$ (50:50 for vol.%).

4. Conclusions
Two series of experiments were performed to obtain SrTiO$_3$ and biphasic SrTiO$_3$−TiO$_2$ ceramics from mixtures of SrCO$_3$ and TiO$_2$ with different component ratios using the reactive SPS method. It has been found that when monophasic ceramics are produced, the mixture is linearly compacted as it is heated, and non-reactive sintering processes are activated from 1000°C to 1100–1200°C. When obtaining biphasic ceramics SrTiO$_3$−TiO$_2$, eutectic melting is observed when the temperature reaches ~1320°C. Partial melting of SrTiO$_3$−TiO$_2$ ceramics sintered at a holding temperature of 1300°C allowed estimating the temperature gradient in the system $\Delta T/\Delta r$~77°/sm. The experimental determination of such parameters is unique. The research of the microstructure of obtained samples allowed determining that the reactive SPS results in the formation of monophasic SrTiO$_3$ and biphasic SrTiO$_3$−TiO$_2$ ceramics of a homogeneous structure with an average grain size of 1–2 µm.

Acknowledgments
This work was supported by the Russian Foundation for Basic Research (Project No. 18-29-11044).

References
[1] Nolas G S, Sharp J and Goldsmid J 2001 Thermoelectrics. Basic Principles and New Materials Developments (Berlin, Heidelberg: Springer) p 293
[2] Raj B (Eds.), Van de Voorde M (Eds.) and Mahajan Y (Eds.) 2017 Nanotechnology for Energy Sustainability (Weinheim, Germany: Wiley-VCH) p 1221
[3] Heremans J P 2005 Acta Phys. Pol. A 108 609–634
[4] Ohta H, Kim S, Mune Y, et al. 2007 Nature Mater. 6 129–134
[5] Zhang R, Wang C and Li J 2010 J. Am. Ceram. Soc. 93 1677–1681
[6] Park N-H, Akamatsu T, Itoh T, et al. 2015 Materials 8 (7) 3992–4003
[7] Zavjalov A, Tikonov S and Kosyanov D 2019 Materials 2 (18) 2895–2925
[8] Safronova N A, Kryzhanovska O S, Dobrotsvorska M V, et al. 2020 Ceram. Int. 46 6537–6543