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Effects of TiB_2 addition on spark plasma sintering and thermoelectric performance of Y-doped $SrTiO_3$ synthesized by polymerized complex process

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ABSTRACT

The Y-doped $SrTiO_3$ + TiB_2 composites were synthesized by polymerized complex process and subsequent spark plasma sintering (SPS). The effects of TiB_2 addition on sintering behavior and control of thermoelectric performance were discussed. When TiB_2 was added, the densification temperature during SPS was significantly reduced by about 200 K. The Seebeck coefficient and electrical resistivity were controllable by changing an amount of TiB_2, as well as the content of Y dopant. The thermal conductivity of Y-doped $SrTiO_3$ + 5 mass% TiB_2 composites was smaller than that of the conventional hot-pressed sample in spite of containing high thermal conductor, TiB_2, because of their finer microstructures due to the SPS process, resulting in the figure of merit larger than the hot-pressed sample.

1. Introduction

Thermoelectric power generation, which can directly convert heat energy into electricity, has been more attractive as a clean means of generating electricity. It can generate electrical energy without any exhaust gases, mechanical vibration, or noise, and there is no maintenance required. Performance of a thermoelectric material is generally evaluated by the dimensionless figure of merit, ZT, which is calculated from the Seebeck coefficient, S, electrical resistivity, ρ, thermal conductivity, κ, and the absolute temperature, T, in the equation $ZT = S^2T/\rho/\kappa$. Generally, thermoelectric oxides can be used at high temperatures without deterioration of their performance due to oxidation, and their production costs are comparatively low. Therefore, several electronic conductive oxides, such as $(Zn_{1-x}Al_x)O$, $BaSrPbO_3$, $Na_xCo_2O_4$, TiO_2-related composites etc., have been recognized as potential candidates for a new thermoelectric material [1–8]. Among them, the p-type thermoelectric oxides, such as $Na_xCo_2O_4$ and $Ca_3Co_4O_9$ etc., are well known to show the high thermoelectric performance [1,9–13]. On the other hand, the thermoelectric properties of the n-type oxides, such as $(Zn_{1-x}Al_x)O$ and $SrTiO_3$ etc., are still low as compared to those of the p-type oxides, and further improvement of the thermoelectric performance of these n-type oxides is required.

In the case of the n-type perovskite $SrTiO_3$ phase, it has been reported that in order to improve the thermoelectric performance, rare-earth metal, such as La, Y, Gd or Pd is partially substituted for Sr site, or Nb is substituted for Ti site [14–23]. In the previous study, we synthesized Y-doped $SrTiO_3$ powders by the polymerized complex process, which is one of the chemical solution processes, like a sol–gel method etc., and then sintered them by hot pressing [24,25]. In this process, the samples needed to be hot-pressed at high temperature, 1673 K, in Ar atmosphere for 2 h, where oxygen deficiency was introduced into the sample in order to reduce electrical resistivity, resulting in the moderate ZT value, 0.146 [25]. On the other hand, it is well known that spark plasma sintering (SPS) is significantly effective for rapid consolidation at lower temperature for shorter sintering time as compared to the conventional sintering process including hot pressing [26–28]. However, when the Y-doped $SrTiO_3$ powders were sintered by SPS (at 1573 K for 5 min), though the powder was well consolidated, the sintered body showed quite large electrical resistivity even when Y was doped to its doping limit (around 10 at%) [24], because of the lower sintering temperature and significantly shorter period of sintering time than those of the hot pressing described above. Thus, it was found that the SPS process was not adequate for synthesizing the thermoelectric $SrTiO_3$ single phase (an unpublished work).

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Generally, the rapid consolidation by SPS process can lead to fine microstructure of a sintered body [29], which is preferable to reduction in thermal conductivity. Therefore, we still expected the SPS process as a promising sintering method for the thermoelectric $SrTiO_3$ polycrystals. As one of methods to reduce electrical resistivity of a powder compact, addition of a good electrical conductor is well recognized. In this study, as a good electrical conductor additive, TiB_2, which has significantly low electrical resistivity about 0.1 μΩm, was added to the Y-doped $SrTiO_3$ powder. The addition of TiB_2 is expected to be beneficial to overcome the problem of SPS synthesis described above. On the other hand, influences of the TiB_2 addition on the thermoelectric performance, such as *ZT*, have not been clarified yet. Based on these facts, Y-doped $SrTiO_3/TiB_2$ composite powders were prepared and sintered via the SPS process in this study. Their thermoelectric properties, *S*, ρ and κ were measured and influences of TiB_2 addition on densification behavior and thermoelectric performance were investigated and discussed. From these results, possibility of the SPS process with TiB_2 addition as a new synthesis route of the thermoelectric $SrTiO_3$ was evaluated.

2. Experimental procedure

2.1. Materials and reagents

All chemicals used in this study were purchased from Wako Pure Chemical Industries, Ltd. and used as received. The average diameter of commercial TiB_2 powder is 1–2 μm according to the data provided by the company.

2.2. Synthesis of Y-doped $SrTiO_3$ powder by polymerized complex process

$SrTiO_3$ thermoelectric oxides were synthesized from a powder precursor prepared by the polymerized complex process. Ti $[OCH(CH_3)_2]_4$ was first dissolved in ethylene glycol and then heated and stirred on a hot stirrer set at 473 K. Subsequently, citric acid ($C_5H_8O_7$), $Sr(NO_3)_2$, and $(CH_3COO)_3Y{\cdot}4H_2O$ were added to this solution. $Sr(NO_3)_2$, $Ti[OCH(CH_3)_2]_4$ and $(CH_3COO)_3Y{\cdot}4H_2O$ were mixed in the mole ratio corresponding to nominal composition of $Sr_{0.95}Y_{0.05}TiO_3$ and $Sr_{0.9}Y_{0.1}TiO_3$. Citric acid and ethylene glycol were mixed in the proportions of 4 mol and 150 mol for each mole of metal cation, respectively. The mixture was then stirred at 473–723 K. During this heating process, the formation of the polymer between ethylene glycol and metal citrate complexes was promoted. As the colloidal solution was condensed, it became highly viscous, and this viscous polymeric product was decomposed to a dark mass precursor at 723 K in air by a mantle heater. This mass precursor was ground and calcined at 1073 K for 36 ks in order to obtain the $SrTiO_3$ phase.

2.3. Preparation of Y-doped $SrTiO_3/TiB_2$ sintered composites by SPS process

In the case of the Y-doped $SrTiO_3/TiB_2$ composites, the calcined powder precursors were mixed with 5 and 10 mass% TiB_2 powder by using a mortar and pestle. The $SrTiO_3$ powder and $SrTiO_3/TiB_2$ powder mixtures were sintered via the SPS apparatus (SPS Syntex Inc., SPS-511S) under a pressure of 40 MPa at 1573 K for 5 min in vacuum. The densification behavior of a powder compact was observed by recording displacement of an upper electrode during sintering, using a data logger attached to the SPS apparatus.

2.4. Characterizations

The phases and the microstructures of these samples were determined by XRD (X-ray diffraction analysis), SEM (scanning electron microscopy) and EDX (energy dispersive X-ray analysis). The XRD analysis was performed on the pressed plane of the sintered compacts using Cu K_α radiation. The density of the sintered bodies was measured by the Archimedes method. The Seebeck coefficient, *S*, and the electrical resistivity, ρ, were simultaneously measured from room temperature to about 1070 K by the ordinary four probe dc method in a flowing Ar gas atmosphere using a computer-controlled equipment, and then the power factor, *P*, of these samples were calculated using *S* and ρ values in the equation $P=S^2/\rho$. The thermal diffusivity, *D*, was measured by the laser flash method using a thermal constant analyzer (ULVAC TC-7000). The heat capacity, C_p, was measured using a differential scanning calorimeter (Shimadzu, DSC-50). The thermal conductivity, κ, was calculated from the measured thermal diffusivity, *D*, heat capacity, C_p, and density, *d*, in the equation $\kappa = D \times C_p \times d$. The dimensionless figure of merit, *ZT*, was calculated using the power factor and the absolute temperature, *T*, in the equation $ZT = PT/\kappa$ $(=S^2T/\rho/\kappa)$.

3. Results and discussion

Fig. 1 shows the XRD patterns of $Sr_{0.9}Y_{0.1}TiO_3$ with 0, 5 and 10 mass% TiB_2 after sintering by SPS. The $SrTiO_3$ single phase of the powder synthesized by polymerized complex process [24] was maintained after SPS, as shown in Fig. 1 (a). When TiB_2 was added, the sintered sample was composed of $SrTiO_3$ and TiB_2 phases only, without formation of any other reacted phase, indicating that $Sr_{0.9}Y_{0.1}TiO_3/TiB_2$ composites were successfully obtained. In the case of the $Sr_{0.95}Y_{0.05}TiO_3$ samples, the XRD patterns of these composites after SPS were almost the same as those in Fig. 1. It has been reported that when TiO_2/SiO_2 composites, TiO_2/ZnO nanorods and Gd–La codoped TiO_2 were synthesized by the hydrothermal method, Si, Zn, Gd and La were partially substituted for Ti ion, respectively [30–33]. On the other hand, in this study, the $SrTiO_3$ powder synthesized by the polymerized complex process was

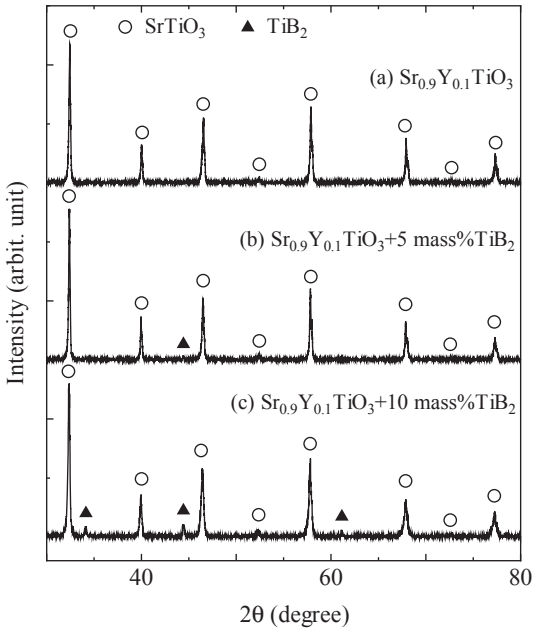

Fig. 1. XRD patterns of the $Sr_{0.9}Y_{0.1}TiO_3$ polycrystals (a)without addition, (b) with 5 mass% TiB_2 and (c) 10 mass% TiB_2.