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Fabrication of Titanium Oxide-Based Composites by Reactive SPS Sintering and Their Thermoelectric Properties

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Titanium oxide-based composites containing (1) Nb, (2) Nb and Sr, and (3) Sr and La were fabricated by a combination of wet processing and reactive spark plasma sintering in which the metal oxide components were reduced by reaction with titanium nitride. If only TiO_2 was used as the starting material, several Magneli-type phases of oxygen-deficient titanium oxides were obtained. When mixed with Nb ions with Ti:Nb = 0.9:0.1, microsegregation of Nb ions was observed (case 1). If Sr was added, a perovskite, $SrTiO_3$ (STO) phase occurred (case 2), which contained La ions in the case of La addition (case 3). The sintered compacts consisted largely of grains of about 1 μm in size. In the case of Ti-Nb combination (case 1), a unique stripe pattern also appeared inside the grains. The electrical conductivity increased monotonically with increasing temperature in the case of the pure Magneli phases and the Nb-containing composite, whereas bow-shaped temperature dependences with a maximum were observed in the case of the composites containing STO phases. The Seebeck coefficients were commonly negative, and the absolute values increased with temperature. The thermal conductivity was between 2 W m^{-1} K^{-1} and 4 W m^{-1} K^{-1} in the temperature range from room temperature to 800°C. A maximum ZT of 0.34 was achieved at 800°C (case 2).

Key words: Titanium oxide, thermoelectric, SPS sintering, microtexture

INTRODUCTION

Oxide thermoelectric (TE) materials have recently drawn special interest due to their thermal stability as well as environmental friendliness. Since the discovery of high TE performance,[1] many oxide materials have been examined.[2] However, it seems that no satisfactory TE property has been found in n-type oxide bulk materials even though Al-doped ZnO[3] and La-doped $SrTiO_3$ (STO)[4] have high TE responses. Recently, it has been reported that some indium oxide-based systems have relatively high TE performance.[5,6] Most recently, Ohta et al.[7] demonstrated that superlattice materials stacking Nb-doped STO and nondoped STO layers could give very large Seebeck coefficients due to two-dimensionally confined electrons. Thereafter, the research group proposed a nanostructured bulk material model based on this finding.[8]

The authors presented another example of STO-based TE materials, namely multiphased oxide composites containing STO and rutile phases.[9] The composites we obtained there had a mosaic-type texture constructed of rutile and STO fine particles with typical size of about 500 nm. Their thermal conductivity values were considerably low, ranging between 2 W m^{-1} K^{-1} and 5 W m^{-1} K^{-1}. However, the maximum ZT value was 0.24 at 600°C, which is lower than that reported for monophase Nb-doped STO polycrystalline compacts.[10] The main inefficiency of our sample seemed to be the lower electrical conductivity. Thus, the next step of our study was to find a way to obtain composites with higher electrical conductivity while maintaining the low thermal conductivity.

For this purpose, we focused our attention on the effect of TiN addition in the sintering process.

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