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High thermoelectric performance of niobium-doped strontium titanate bulk material affected by all-scale grain boundary and inclusions

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The large thermal conductivity of $SrTiO_3$ bulk material limits its potential application for high-temperature thermoelectricity. The effects of all-scale grain boundaries and inclusions on the thermoelectric performance of Nb-doped bulk $SrTiO_3$ materials are investigated in this study. Nano- to microscale grain boundaries and inclusions reduce the thermal conductivity by 30%. As a result, the ZT value is enhanced 2.6 times by a combination of all-sized crystals, energy filtering effect, multilevel scattering behaviors of nano/microscale grain boundaries and inclusions.

Keywords: Thermoelectric; Niobium-doped strontium titanate; All-scale grain boundary; Molten salt synthesis

Thermoelectric materials have attracted much attention because they can directly and reversibly convert heat into electrical energy. However, their applications are limited by their low thermoelectric dimensionless figure of merit, ZT. Efficient thermoelectric materials are generally characterized by a high ZT. According to the equation $ZT = S^2\sigma T/k$ (where S, σ, k and T are the Seebeck coefficient, electrical conductivity, thermal conductivity and working temperature, respectively), a high ZT can be obtained by increasing S and/or σ, and decreasing k.

Although some alloy materials, e.g. Bi_2Te_3 [1,2], Zn_4Sb_3 [3] and $Cu_{2-x}Se$ [4], exhibit high thermoelectric performance, the use of rare or toxic elements in these compounds limits their large-scale commercial application. Compared with alloys, oxide materials offer a number of advantages, including good thermal stability, environmental friendliness, low-cost preparation process and a range of chemical compositions. $SrTiO_3$, a typical perovskite oxide, with its excellent properties such as high chemical and thermal stability, and low toxicity, has potential for high-temperature thermoelectric applications. Further, the relatively high carrier concentration and large effective mass of electron-doped $SrTiO_3$ results in high electric conductivity as well as a high Seebeck coefficient [5]. For example, its power factor is large compared to that of standard alloy materials obtained from Nb- and La-doped $SrTiO_3$ [5,6]. Although Nb-doped $SrTiO_3$ thin film containing a high-density two-dimensional electron cloud exhibited high ZT at room temperature [7], existing $SrTiO_3$ bulk materials have a small ZT because of their large k value. Accordingly, much research has focused on enhancing the ZT of $SrTiO_3$ bulk materials. A study on the effect of grain boundaries of single-crystalline epitaxial film, polycrystalline film and ceramic samples of 20% Nb-doped $SrTiO_3$ on their Seebeck coefficient and carrier concentration has shown that the ZT does not depend on the grain size at 1000 K (0.35) [8]. The Seebeck coefficient has been increased by doping with Nb at the grain boundaries of La-doped $SrTiO_3$ nanoceramics at temperatures of 300–800 K [9]. The addition of mesoporous silica can enhance the ZT significantly due to the reduction of the thermal conductivity and the enhancement of the electrical conductivity [10]. Yttria-stabilized zirconia nano-inclusions are effective at increasing the electrical conductivity and decreasing the thermal conductivity [11]. Nanostructured La-doped $SrTiO_3$ ceramic produced by spark plasma sintering (SPS) exhibited a relatively high ZT of 0.37 at 973 K [12]. On the other hand, for alloy materials, the thermoelectric performance of PbTe alloy has been significantly enhanced by considering sources of scattering to be atomic-scale lattice disorder, nanostructures and grain boundaries in a hierarchical fashion [13]. This method has the potential to increase the thermal performance of oxide bulk materials for practical applications.

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Table 1. Synthesis conditions for the powder samples.

Raw materials (Oxide)/flux (Salt)	Ratio of reagents (O/S ratio)	Heating time (h) at 1250 °C	Power samples name	Dish samples name
$Sr(NO_3)_2$: TiO_2: Nb_2O_5: NaCI: KCI	1:0:8:0.2:2.5:2.5(2:5)	5	P1	D1
$Sr(NO_3)_2$: TiO_2: Nb_2O_5: NaCI	1:0:8:0.2:1:1(1:1)	18	P2	D2

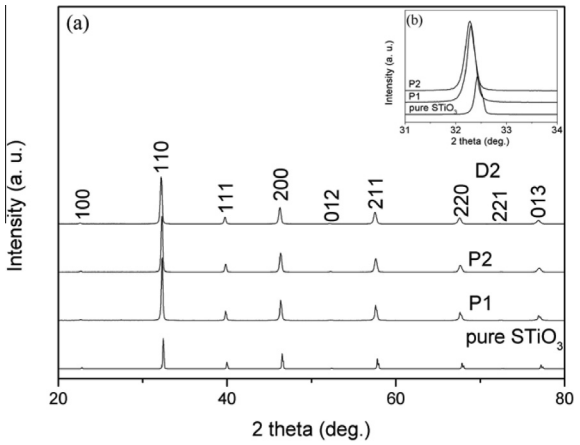

Figure 1. (a) XRD patterns of P1, P2 and D2, together with pure $SrTiO_3$. (b) An enlargement of 110 peaks for P1, P2 and pure $SrTiO_3$.

In this study, therefore, 20% Nb-doped STO powder with grain sizes ranging from the nano- to microscale were synthesized by a molten salt synthesis (MSS) method, and dish-shaped ceramic samples contained nano/micrometer-scale grain boundaries were prepared by SPS. The thermal performance was discussed by analyzing the combined effect of all-sized crystals, energy filtering, and the multilevel scattering behavior of nano/micrometer-scale grain boundaries on the electrical conductivity, Seebeck coefficient and thermal conductivity.

Nb-doped nano/micrometer-scale powders were synthesized by MSS. $Sr(NO_3)_2$, TiO_2, Nb_2O_5 (raw materials, oxide) and flux (salt) were mixed in 1:0.8:0.2:x (x = 2 or 5) molar ratio and milled by a mortar. The fluxes used in the study were a 1:1 M ratio mixture of KCl and NaCl, or NaCl alone. The mixture of raw materials and flux was milled by a mortar for a few minutes, placed into an alundum crucible and then heat treated at 1250 °C for 5 or 18 h. The reaction product was washed repeatedly with deionized water in order to dissolve the flux completely. The powders were dried in a drying cabinet at 120 °C. The obtained powder samples were hot pressed into dish-shaped samples by SPS at 65 MPa. As shown in Table 1, Nb-doped $SrTiO_3$ powders synthesized by 2:5 and 1:1 oxide/flux (O/S) molar ratios are abbreviated to P1, P2 and the dish samples are D1, D2, respectively.

X-ray diffraction (XRD) was used to identify the generation of $SrTIO_3$, and scanning electron microscopy (SEM; JSM7000F, JEOL Ltd.) was employed to observe morphology and size of particles. Energy-dispersive spectrometry (EDS) was used to analyze the chemical composition and retained flux in the product. The Seebeck coefficient and electrical conductivity were measured at 300–1100 K in a He atmosphere using a thermoelectric analysis apparatus (ZEM-3, ULVAC-RIKO, Japan). Thermal diffusivity (α) was measured by a standard laser flash method (TC9000, Ulvac-Rico, Japan). Thermal conductivity was calculated from the specific heat capacity (c_p) [14], thermal diffusivity (α) and experimental density (ρ) of $SrTiO_3$ by using the equation $k = \alpha\ c_p\ \rho$.

Figure 1a illustrates the powder XRD patterns of P1, P2 and D2, together with the data of cubic perovskite structure pure $SrTiO_3$ for comparison. The peak position and relative intensity of all diffraction peaks for P1, P2 and D2 match well with the diffraction data of pure $SrTiO_3$. In Figure 1b the peak positions shift left for all diffraction peaks after doping with Nb, indicating that the larger-sized Nb^{5+} ions have replaced the smaller-sized Ti^{4+} ions in the b-sites of

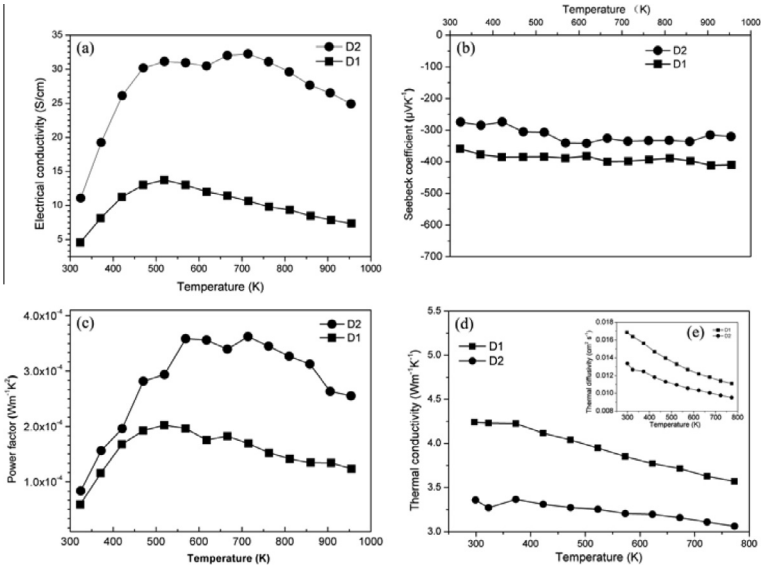

Figure 2. Temperature dependence of electrical conductivity (a), Seebeck coefficient (b), power factor (c), thermal conductivity (d) and thermal diffusivity (e) for D1 and D2.