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Enhanced thermoelectric performance of Nb-doped SrTiO₃ by nano-inclusion with low thermal conductivity

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Authors reported an effective path to increase the electrical conductivity while to decrease the thermal conductivity, and thus to enhance the ZT value by nano-inclusions. By this method, the ZT value of Nb-doped SrTiO₃ was enhanced 9-fold by yttria stabilized zirconia (YSZ) nano-inclusions. YSZ inclusions, located inside grain and in triple junction, can reduce the thermal conductivity by effective interface phonon scattering, enhance the electrical conductivity by promoting the abnormal grain growth, and thus lead to the obvious enhancement of ZT value, which strongly suggests that, it is possible to not only reduce the thermal conductivity, but also increase the electrical conductivity by nano-inclusions with low thermal conductivity. This study will give some useful enlightenment to the preparation of high-performance oxide thermoelectric materials.

Thermoelectric (TE) energy conversion is a promising technology for both electricity power generation in harvesting wasted heat and electric cooling. The efficiency of TE devices is characterized by the dimensionless figure of merit, $ZT = (S^2\sigma/\kappa)T$, where S , σ , κ , and T are the Seebeck coefficient, the electrical conductivity, the thermal conductivity, and the absolute temperature, respectively. To date, most of the discovered bulk materials with high ZT values exhibit thermal and chemical instability in air, and are composed of toxic, scarce or expensive elements^{1–5}. Recently, various ceramic oxide thermoelectric (TE) materials have attracted widespread attention, because they are economical, environmentally-friendly, possess various chemical compositions, and consist of naturally abundant^{6–14}. So far, among the p -type oxide thermoelectric bulk materials, the textured BiCuSeO has the highest ZT value, ~ 1.4 at 923 K¹⁵, which can meet the basic requirements of practical applications. Both p -type and n -type oxide materials are needed to construct an efficient thermoelectric device. However, among the n -type oxide thermoelectric bulk materials, even though Nb-doped SrTiO₃ bulk ceramic has the highest ZT value so far¹⁶, but it is still very low, compared with p -type textured BiCuSeO, and thus urgently needs to improve.

In 2007, Dresselhaus *et al.* proposed that nanocomposite thermoelectric materials would offer a promising approach for the preparation of bulk samples with nano-sized constituents¹⁷. Since then, a variety of nanocomposites with higher thermoelectric properties than bulk materials have been prepared. Tang *et al.* prepared Bi₂Te₃ bulk materials with layered nanostructure by combining melt spinning technique with spark plasma sintering, and the maximum ZT value of 1.35 was obtained at 300 K¹⁸. Mi *et al.* prepared n -type CoSb₃ nanocomposites by hot pressing the mixture of nanoscale and micro-sized CoSb₃ powders, and the maximum ZT value reached 0.71 at 700 K¹⁹. Poudel *et al.* fabricated nano-sized bismuth antimony telluride bulk alloys by ball milling and hot pressing method, and the obtained maximum ZT value was 1.4 at 373 K²⁰. Li *et al.* fabricated Yb_{0.2}Co₄Sb_{12+y} bulk materials with nanostructure by combining melt spinning technique with spark plasma sintering, and the maximum ZT value reached 1.26 at 800 K²¹. Li *et al.* also prepared n -type skutterudites In_xCe_yCo₄Sb₁₂ with in-situ forming nano-sized InSb phase by a melt-quench-anneal-spark plasma sintering method, and the maximum ZT value of 1.43 was obtained at 800 K²². Lan *et al.* found that small nanosized particles located at the grain boundaries or embedded in larger particles could provide effective phonon scattering centers and thus reduced the phonon thermal conductivity efficiently²³. Pei *et al.* found that there was an enhancement of ZT due to phonon scattering at the interfaces, when PbTe was nanostructured with large nanometer sized Ag₂Te precipitates²⁴. Ahn *et al.* prepared p -type PbTe-MTe ($M = \text{Cd, Hg}$) and found that meso-scale grain boundaries along with nanostructured precipitates play an important role in significantly reducing the lattice thermal conductivity²⁵. Above-mentioned studies on thermoelectric materials with nanocomposite gave us some good inspirations.

Herein, we reported an effective path to enhance the thermoelectric performance of *n*-type oxide, Nb-doped SrTiO₃ (SrNb_{0.15}Ti_{0.85}O₃, Nb-STO), by yttria stabilized zirconia (YSZ) nano-inclusion with the low thermal conductivity. Our results show the *ZT* value of Nb-STO was enhanced 9-fold, due to the decreased thermal conductivity and meanwhile the increased electrical conductivity, pointing to a robust approach for high-performance *n*-type thermoelectric oxide.

Results

Fig. 1 showed the temperature dependent thermal and electric transport properties of YSZ/Nb-STO composite, namely, the thermal conductivity (κ), electrical conductivity (σ), and Seebeck coefficient (S). Significantly, YSZ inclusion reduced the thermal conductivity (Fig. 1(a)), and meanwhile increased the electrical conductivity (Fig. 1(b)). However, Seebeck coefficients were subjected to a very small impact by YSZ inclusion (Fig. 1(c)). The thermal conductivity and the electrical conductivity at 900 K were reduced $\sim 15\%$ and increased 10-fold, respectively.

Fig. 2 showed the temperature dependent electrical conductivity and thermal conductivity of pure YSZ bulk ceramic, with the relative density of 91.6%, prepared by the conventional normal pressure sintering method at 1500°C for 3 h in an Ar atmosphere. The thermal conductivity and the electrical conductivity of YSZ bulk were much lower than those of pure Nb-STO ceramic showed in Fig. 1(a) and Fig. 1(b).

The thermoelectric power factor $S^2\sigma$ and dimensionless figure of merit ZT of the composite were shown in Fig. 3. The power factor was increased more than 7-fold as compared with the sample without YSZ inclusion (Fig. 3(a)), which is mainly beneficial from the increased electrical conductivity. Owing to the low thermal conductivity and high electrical conductivity, the ZT value is enhanced 9-fold, up to 0.21 at 900 K.

Discussion

The carrier concentration (n), Hall mobility (μ), carrier effective mass (m^*/m_0) and $m^*/n^{2/3}$ at room temperature were summarized in the Table 1. With YSZ inclusion, the mobility was enhanced significantly, however, relatively, there was little change in the carrier concentration, which contributed to the enhancement of the electrical conductivity, according to the relation formula:

$$\sigma = ne\mu. \quad (1)$$

For degenerate semiconductors (parabolic band, energy-independent scattering approximation), the Seebeck coefficient (S) is given by²⁶:

$$S = (8\pi^2 k_B^2 / 3eh^2) m^* T (\pi / 3n)^{2/3}, \quad (2)$$

where k_B is Boltzmann constant and h is Planck constant. The equation indicates the Seebeck coefficient strongly depends on the value, $m^*/n^{2/3}$. Table 1 exhibited YSZ inclusion had very small impact on the value, $m^*/n^{2/3}$, which led to that Seebeck coefficient was almost independent of YSZ inclusion.

Temperature dependent electronic thermal conductivity (κ_e), lattice thermal conductivity (κ_L) and phonon mean free path (L_{phonon}) of YSZ/Nb-STO composites were shown in Fig. 4. The κ_e was subtracted from the total thermal conductivity by using the Wiedemann-Franz law:

$$\kappa_e = LT\sigma, \quad (3)$$

where L is the Lorenz factor, $2.45 \times 10^{-8} \text{ V}^2/\text{K}^2$. The resulting κ_L was obtained by the relation:

$$\kappa_e = \kappa - \kappa_L. \quad (4)$$

L_{phonon} was evaluated by the following equations^{27,28},

Figure 1 | Temperature dependent thermal and electric transport properties of YSZ/Nb-STO composite. (a) thermal conductivity (κ), (b) electrical conductivity (σ), and (c) Seebeck coefficient (S).

$$L_{\text{phonon}} = 3\kappa_L / \left[3^{1/3} C (1/V_L^3 + 2/V_S^3)^{-1/3} \right], \quad (5)$$

where V_L , V_S , C , were the longitudinal sound velocity, transverse sound velocity and specific heat capacity, respectively. Fig. 4(c) revealed that YSZ inclusion significantly decreased L_{phonon} and further induced the reduction in κ_L (Fig. 4(b)).

Scanning electron micrographs (SEM) of YSZ/Nb-STO composite (Fig. 5(a) and (b)) showed the grain size was increased obviously by YSZ inclusion. To confirm where YSZ existed in bulk Nb-STO

Figure 2 | Temperature dependent electrical conductivity and thermal conductivity of pure YSZ bulk ceramic.

ceramic, transmission electron microscope (TEM) observation and selected area electron diffractions (SAED) were carried out. The SAED patterns in Fig. 5(c-ii) and Fig. 5(d-ii), taken from large crystalline area in Fig. 5(c) and Fig. 5(d), were only well-matched with a cubic strontium titanate crystal. However, the SAED patterns in

Figure 3 | Temperature dependent thermoelectric power factor $S^2\sigma$ (a) and dimensionless figure of merit ZT (b) of YSZ/Nb-STO composite.

Table 1 | Carrier concentration (n), Hall mobility (μ), carrier effective mass (m^*/m_0 , m_0 = free electron mass) and $m^*/n^{2/3}$ at room temperature

	n (10^{21} cm^{-3})	μ ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	m^*/m_0	$m^*/n^{2/3}$ (10^{-14} cm^2)
Pure Nb-STO	1.57 [†]	8×10^{-4}	1.75	1.29 m_0
YSZ/Nb-STO	2.06	6.11	2.16	1.27 m_0

[†]estimated using the lattice constant and relative density (63.1%) of pure Nb-STO.

Fig. 5(c-i) and Fig. 5(d-i), taken from black nano-sized particles in Fig. 5(c) and Fig. 5(d), revealed some diffraction spots except the diffraction spots of strontium titanate, which matched the diffraction spots of YSZ very well. Above-mentioned evidences fully proved that YSZ inclusions located inside the grain (Fig. 5 (c)) and in the triple junction (Fig. 5(d)), and these inclusions were nano-sized, from several tens nanometers to several hundreds nanometers. YSZ has much lower thermal conductivity, $\sim 2.5 \text{ Wm}^{-1} \text{ K}^{-1}$ below 1200 K ²⁹, compared with SrTiO_3 ³⁰. YSZ nano-inclusions inside the grain and in the triple junction could scatter the phonons effectively and thus brought about the decrease in the phonon mean free path, the lattice thermal conductivity and the total thermal conductivity, in sequence. As for SrTiO_3 ceramic with oxide additives, such as TiO_2 , Al_2O_3 and SiO_2 , at the sintering temperature of over than 1400°C , the liquid phase formed at triple grain junctions and exhibited complete wetting of the grain boundaries³¹. YSZ/Nb-STO sample exhibited the abnormal grain growth in our experiment, which could be a similar liquid phase sintering behavior to SrTiO_3 ceramic with added TiO_2 , Al_2O_3 and SiO_2 in Ref. 31. According to the liquid-phase sintering theory proposed by Kingery³², the liquid phase formation could lead

Figure 4 | Temperature dependent electronic thermal conductivity (κ_e) (a), lattice thermal conductivity (κ_l) (b) and phonon mean free path (L_{phonon}) (c) of YSZ/Nb-STO composite.

Figure 5 | Microstructures and SAED patterns of YSZ/Nb-STO composite. (a) SEM of sample without YSZ inclusion; (b) SEM of sample with YSZ inclusion; (c) TEM of sample with YSZ inclusion inside grain; (d) TEM of sample with YSZ inclusion in triple junction; (c-i) SAED pattern taken from i-area in Fig. 5(c); (c-ii) SAED pattern taken from ii-area in Fig. 5(c); (d-i) SAED pattern taken from i-area in Fig. 5(d); (d-ii) SAED pattern taken from ii-area in Fig. 5(d).

to the complete wetting of the grain boundaries, increase the grain boundary mobility and thus markedly accelerate the sintering rate and grain growth. The abnormal crystal growth of strontium titanate grain could obviously diminish the number density of grain boundaries and further reduce interface scattering of electrons remarkably, which partly contributed to the increased mobility and further to the enhanced electrical conductivity. On the other hand, Compared with pure Nb-STO, the relative density of YSZ/Nb-STO composite was increased from 63.1% to 79.4%, which was also partly contributed to the enhanced electrical conductivity. Fig. 6 showed the interaction schematic of phonon-nano-inclusion and electron-nano-inclusion.

In summary, YSZ nano-inclusion could effectively reduce the thermal conductivity and increase the electrical conductivity of Nb-STO, and thus obviously enhance the ZT value, which strongly suggested that oxide nano-inclusion with low thermal conductivity could be an effective strategy to enhance the thermoelectric properties of oxide thermoelectric materials with high thermal conductivity. Oxide nano-inclusion distributed inside the grain and in the triple junction can obviously reduce the phonon mean free path by the effective interface phonon scattering, and further apparently lead

Figure 6 | Schematic of phonon-nano-inclusion interaction and electron-nano-inclusion interaction.

to the decrease in the thermal conductivity. Meanwhile, the oxide nano-inclusion with high surface activation can promote the grain growth, diminish the number density of grain boundaries, increase relative density and thus improve the carrier mobility and the electrical conductivity. Our research may give some helpful enlightenment to develop high-performance oxide thermoelectric materials.

Methods

Sample preparation. Commercial YSZ (8 mol% yttria-stabilized zirconia) particles with the size of 25 ~ 30 nm were used as an oxide inclusion. Nb-doped SrTiO₃ ceramic sample with YSZ inclusion of 3 wt% were fabricated by the conventional normal pressure sintering method at 1500°C for 3 h in an Ar atmosphere. The relative densities of Nb-doped SrTiO₃ ceramic without added YSZ and with YSZ inclusion of 3 wt% are 63.1% and 79.4%, respectively.

Sample characterization. The thermoelectric performances, such as the Seebeck coefficient and electrical conductivity, were measured at 300–900 K in an Ar atmosphere by using an automatic thermoelectric measuring apparatus (Ozawa RZ2001K). The thermal diffusivity was measured by the usual laser flash method (ULVAC-RIKO TC-9000V). The carrier concentration and mobility was measured by the Van der Pauw's method (RESITEST 8300). The microstructures were observed on a scanning electron microscope (SEM) and a JEM-2010 transmission electron microscope (TEM). The specific heat capacity was measured by a differential scanning calorimeter system (TA Instrument DSC-2910). The mean phonon velocity was measured by an ultrasonic pulse-echo method (Panametrics-NDT 5800). The electrical properties (electrical conductivity and Seebeck coefficient) and thermal conductivity were measured in in-plane and cross-plane directions. YSZ/Nb-STO polycrystalline ceramic composite exhibited the isotropic electrical conductivity, Seebeck coefficient and thermal conductivity.

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Author contributions

N.W. and K.K. designed the experiments. N.W. carried out the fabrication of materials and thermoelectric measurements. W.N. and M.K. contributed to microstructural characterizations. H.J.C. and H.C.H. provided helps in the experiments. N.W. and H.J.C. wrote the paper, and all authors reviewed the manuscript.

Additional information

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