



# Enhanced thermoelectric performance of highly dense and fine-grained $(\text{Sr}_{1-x}\text{Gd}_x)\text{TiO}_{3-\delta}$ ceramics synthesized by sol–gel process and spark plasma sintering



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## ABSTRACT

Highly dense and fine-grained  $(\text{Sr}_{1-x}\text{Gd}_x)\text{TiO}_{3-\delta}$  ceramics ( $x = 0.05\text{--}0.12$ ) were fabricated by a sol–gel process plus spark plasma sintering, and their thermoelectric properties were investigated from  $\sim 300$  K to 1100 K. The results show that the electrical resistivity of the  $(\text{Sr}_{1-x}\text{Gd}_x)\text{TiO}_{3-\delta}$  ceramics decreases greatly while maintaining large absolute value of the Seebeck coefficient  $|S|$  upon Gd doping. As a result, a large power factor ( $PF$ ) greater than  $10 \mu\text{W cm}^{-1} \text{K}^{-2}$  is obtained in  $(\text{Sr}_{0.9}\text{Gd}_{0.1})\text{TiO}_{3-\delta}$  in the temperature range from 400 K to 1000 K, and peak  $PF$  reaches  $16 \mu\text{W cm}^{-1} \text{K}^{-2}$  at  $\sim 570$  K. Simultaneously, the lattice thermal conductivity  $\kappa_L$  reduces remarkably (e.g.  $\kappa_L$  decreases from 2.7 to  $2.13 \text{ W m}^{-1} \text{K}^{-1}$  at  $\sim 1000$  K). Owing to the large  $PF$  and low  $\kappa_L$ , a record value of figure of merit  $ZT = 0.37$  is achieved at 1006 K for  $(\text{Sr}_{0.9}\text{Gd}_{0.1})\text{TiO}_{3-\delta}$ , indicating that appropriate combinations of fine-grained microstructure with both high densities and proper doping as well as oxygen deficiency are essential to the effective enhancement of thermoelectric performance of STO-based ceramics.

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## 1. Introduction

Thermoelectric (TE) materials have attracted much interest due to their potential applications in the conversion between thermal and electrical energy [1]. Generally, the efficiency of a TE material is evaluated by the dimensionless figure of merit, defined as  $ZT = S^2T/\rho\kappa$ , where  $S$ ,  $\rho$ ,  $\kappa$  and  $T$  are the Seebeck coefficient, electrical resistivity, total thermal conductivity and absolute temperature, respectively. It is clear that a relatively large power factor  $PF$  ( $S^2/\rho$ ) with a low value of  $\kappa$  is desirable to achieve a better TE performance. Conventional heavy-metal-based solid materials have higher  $ZT$  values, including  $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$  ( $ZT = 1.39$  at 390 K) [2],  $(\text{Bi}_{0.001}\text{Pb}_{0.999}\text{Te})_{0.88}(\text{PbS})_{0.12}$  ( $ZT = 1.20$  at 573 K) [3], etc. However, the low thermal decomposition temperature with toxic heavy metals restricts the applicabilities at high temperatures. With respect to high-temperature TE materials, considerable efforts have been made on metal oxides because of their lower cost, excellent thermal and chemical stabilities [4–8]. Among bulk oxides, p-type TE materials, such as  $\text{Ca}_{2.7}\text{Ag}_{0.3}\text{Co}_4\text{O}_9/\text{Ag}$ -10 wt.% ( $ZT = 0.5$  at 1000 K) [6],  $\text{Bi}_{0.875}\text{Ba}_{0.125}\text{CuSeO}$  ( $ZT = 1.1$  at 923 K) [7], are well known to exhibit a rather better performance. Nevertheless, the TE properties of n-type bulk oxides such as electron-doped

$\text{CaMnO}_3$  and  $\text{ZnO}$  are still low as compared to those of the p-type bulk oxides [4,8].

To date, electron-doped  $\text{SrTiO}_3$  (STO) is still considered as a promising n-type TE oxide in high temperature range. Because of the large Seebeck coefficient even in a heavily carrier doped state, the  $PF$  of this material was reported to be as large as  $13\text{--}15 \mu\text{W cm}^{-1} \text{K}^{-2}$  at 1000 K [9]. Many methods have been investigated to fabricate the electron-doped STO polycrystalline oxides, such as solid-state reaction (SSR) [10–14], hydrothermal method [15], combustion synthesis (CS) [16] and sol–gel method with post spark plasma sintering (SPS) [17]. The molecular-scale mixing of cations in the sol–gel process can prepare oxide at a relatively lower sintering temperature (1203 K), and the rapid densification of SPS would benefit the fabrication of highly dense compounds in a short time with ultra-fine grain sizes ( $\sim 300$  nm) [17]. The  $\kappa$  for  $(\text{Sr}_{0.92}\text{La}_{0.08})\text{TiO}_3$  was decreased to the minimum of  $1.19 \text{ W m}^{-1} \text{K}^{-1}$  at 773 K due to the enhanced phonon scattering at the grain boundaries [17]. However, due to the poor electrical conductivity, the maximum  $ZT$  (0.08 at 679 K) was significantly lower than that (0.37 at 1045 K) of the high dense sample (97.7% theoretical density) prepared by CS with post-SPS [16]. Obviously, one should focus on not only reduction in  $\kappa$  but also maintaining a high  $PF$  so as to improve the TE performance. This means that optimal combinations of grain sizes (volume fraction of grain boundaries) and densifications should be realized and proper element doping with additional donor-type oxygen vacancies

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should be introduced (to provide additional itinerant carriers to the conduction band) in order to improve the thermoelectric performance of the STO-based oxides [11]. In this study, we combined the sol–gel process with SPS to prepare highly dense and fine-grained Gd-doped STO ceramics,  $(\text{Sr}_{1-x}\text{Gd}_x)\text{TiO}_{3-\delta}$  (here  $\delta$  is the oxygen deficiency), with an emphasis on the effects of Gd doping on thermoelectric properties of STO system. Since the substitution of  $\text{Gd}^{3+}$  for  $\text{Sr}^{2+}$  will increase effectively electron concentration, and larger mass of Gd than that of La could effectively lower the  $\kappa$  of STO due to larger mass fluctuation effect [18], the proper Gd-doped compounds  $(\text{Sr}_{1-x}\text{Gd}_x)\text{TiO}_{3-\delta}$  with fine-grained microstructures are expected to possess high TE performances.

## 2. Experimental procedures

Powders of  $(\text{Sr}_{1-x}\text{Gd}_x)\text{TiO}_3$  ( $x = 0, 0.05, 0.08, 0.10, 0.12$ ) were prepared by a citrate sol–gel method. The mixture of  $\text{Sr}(\text{NO}_3)_2$  (99.5%),  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (99.99%, aladdin, China) were dissolved in proper de-ionized water, and appropriate molar ratio of citric acid monohydrated (99.5%, Sinopharm Chemical Reagent Co., Ltd, China) was then added to this solution without any pH adjustment. Subsequently, the tetrabutyl titanate (99%, Sinopharm Chemical Reagent Co., Ltd, China), alcohol and ethylene glycol were blended in the 1:20:1 M ratio, then the mixture was slowly dropped into the above solution with continuously stirring at 343 K until a viscous sol was formed (Sr:Gd:Ti in the desired ratios, and the total metal cations: citric acid molar ratio = 1:2.5–3). The obtained sol was first aged at 343 K for one day to form a complete viscous gel, and then dried at 453 K for 6 h to promote polymerization. After removing excess solvents, a deep brown and porous solid mass (zero gel) was formed. Then the  $(\text{Sr}_{1-x}\text{Gd}_x)\text{TiO}_3$  powders were obtained by calcining the zero gel at 1223 K in air for 6 h.

In order to introduce more oxygen vacancies, the synthesized  $(\text{Sr}_{1-x}\text{Gd}_x)\text{TiO}_3$  powders were annealed at 1473 K for 2 h in a reducing atmosphere (flow rate: 300 ml/min) of mixture of Ar and  $\text{H}_2$  gases (5 vol.% hydrogen in argon). Finally, the high-density ceramic samples  $(\text{Sr}_{1-x}\text{Gd}_x)\text{TiO}_{3-\delta}$  were sintered by SPS for 5 min at 1648 K under a pressure of 40 MPa with a heating/cooling rate of 100 K/min in an Ar flow.

Thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses of the zero gel were performed simultaneously in air by a SDTQ600 instrument with a heating rate of 10 K/min from room temperature to 1273 K. The phase structures of the samples were investigated by X-ray diffraction (XRD, Philips X'pert PRO) with  $\text{Cu K}\alpha$  radiation, and the lattice parameters were calculated from the XRD patterns by using a Si standard for calibration. The oxygen deficiency content  $\delta$  in the sintered samples was estimated by measuring the weight increase after heating at 1373 K in oxygen flow for 24 h. The  $(\text{Sr}_{1-x}\text{Gd}_x)\text{TiO}_{3-\delta}$  bulk samples were polished and thermal-etched in vacuum at 1373 K for 10 min, and the surface morphologies were observed by field emission scanning electron microscope (FESEM, Sirion 200 FEI). The  $\rho$  and  $S$  for the samples were measured simultaneously using a ZEM-3 equipment (Ulvac Riko, Inc.) in helium atmosphere. Thermal diffusivity  $D$  and specific capacity  $C_p$  were measured by a laser-flash method (Netzsch, LFA 457) and differential scanning calorimetry (DSC, Perkin–Elmer), respectively. Archimedes method was used to measure the density  $\lambda$  of bulk samples and the total thermal conductivity  $\kappa$  was calculated from the formula  $\kappa = DC_p\lambda$ .

## 3. Results and discussion

The TG–DSC curves of the 5 at.% Gd-doped STO zero gel are shown in Fig. 1. In consideration of the zero weight loss above 1223 K from TG curve, the  $(\text{Sr}_{0.95}\text{Gd}_{0.05})\text{TiO}_3$  powders were obtained by calcining the zero gel at 1223 K in air for 6 h. Fig. 2a shows the XRD patterns of the  $(\text{Sr}_{0.95}\text{Gd}_{0.05})\text{TiO}_3$  powders sintered in air ( $a_1$ ), annealed powders (before SPS,  $a_2$ ) and ceramic sample (after SPS,  $a_3$ ), respectively. It can be seen that all of the diffraction peaks for the samples can be indexed cubic STO (JCPDS No. 35-0734), and no detectable impurity peaks are observed in XRD patterns, which indicates that not only the powders obtained at 1223 K, but also the samples sintered by SPS are pure phase of STO. The results show that the combination of the sol–gel method and SPS can lower the sintering temperature so that fine grain sizes with high densification can be obtained (for details see the text below), which is superior to the conventional solid-state reaction (SSR) method ( $T > 1733$  K) to prepare the STO-based oxides [10–12].

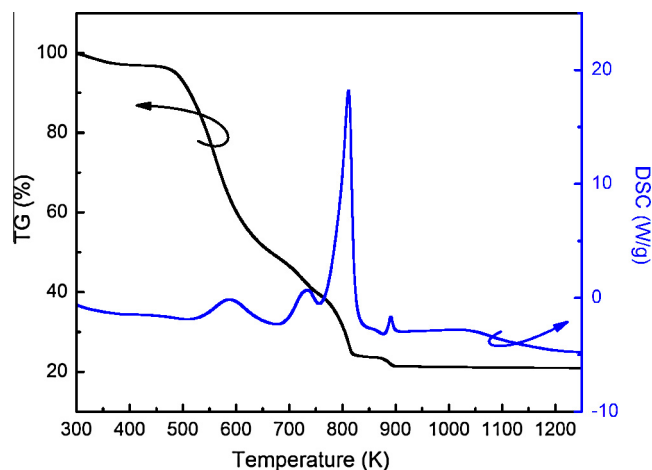


Fig. 1. TG–DSC curves of the  $(\text{Sr}_{0.95}\text{Gd}_{0.05})\text{TiO}_3$  zero gel.

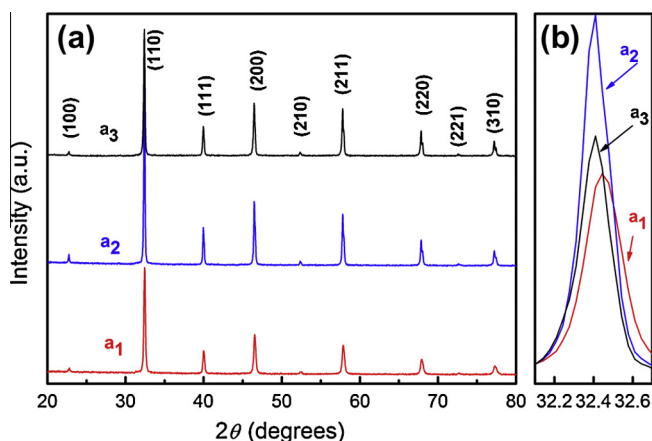


Fig. 2. XRD patterns of (a) the  $(\text{Sr}_{0.95}\text{Gd}_{0.05})\text{TiO}_3$  before and after SPS and (b) the enlarged (110) peaks:  $a_1$ ,  $a_2$ , and  $a_3$  correspond to the sintered powders in air, the annealed powders (before SPS) and the ceramic sample (after SPS).

The introduction of oxygen vacancies could significantly improve the electronic transport properties of the Gd-doped STO materials by increasing the carrier concentration. The lattice oxide ions are removed by the reduction of the samples, which can be expressed by the following equation:



Meanwhile, a corresponding amount of  $\text{Ti}^{4+}$  is believed to be reduced to  $\text{Ti}^{3+}$  with larger ionic radius to keep the charge equilibrium [19], which explains why the diffraction peaks of the reduced samples shift slightly to the lower diffraction angles, as shown in Fig. 2b

The room-temperature XRD patterns of the  $(\text{Sr}_{1-x}\text{Gd}_x)\text{TiO}_{3-\delta}$  ceramics with different Gd contents  $x$  are shown in Fig. 3. It can be seen that all the  $(\text{Sr}_{1-x}\text{Gd}_x)\text{TiO}_{3-\delta}$  samples have the same single phase. However, the lattice constant  $a$  decreases as the Gd content increases due to the substitution of  $\text{Gd}^{3+}$  for  $\text{Sr}^{2+}$ , as listed in Table 1, for the ionic radius of  $\text{Gd}^{3+}$  is slightly smaller than that of  $\text{Sr}^{2+}$  [20]. The relative densities of all samples after SPS are 98.6%, 99.0%, 99.1%, 98.7% and 97.8% for  $x = 0, 0.05, 0.08, 0.10$ , and 0.12, respectively, indicating that highly dense bulk samples are successfully fabricated.

FESEM micrographs of the thermal-etched surfaces for  $(\text{Sr}_{1-x}\text{Gd}_x)\text{TiO}_{3-\delta}$  samples are shown in Fig. 4. There are only a few pores can be detected in the surfaces for all doped samples,

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