Thermal conductivity reduction in oxygen-deficient strontium titanates

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We report significant thermal conductivity reduction in oxygen-deficient lanthanum-doped strontium titanate ($Sr_{1-x}La_xTiO_{3-\delta}$) films as compared to unreduced strontium titanates. Our experimental results suggest that the oxygen vacancies could have played an important role in the reduction. This could be due to the nature of randomly distributed and clustered vacancies, which would be very effective to scatter phonons. Our results could provide a pathway for tailoring the thermal conductivity of complex oxides, which is very beneficial to various applications including thermoelectrics. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2930679]

Solid-state thermoelectric systems are very attractive due to many advantages over conventional energy conversion systems. For example, they can be operated with various types of energy sources and in either refrigeration or power generation mode. Furthermore, they can be made either large or small due to simpler leg-type structures than those of conventional systems that require hazardous working fluid and/or complicated moving parts. Consequently, thermoelectric systems are extremely promising for a variety of applications including cooling systems for the management of problematic local heating in the state-of-the-art microprocessors and optical components, and power generation systems for the waste heat recovery systems of power plants and hybrid automobiles. However, current thermoelectric materials based on bismuth telluride and semiconductors do not provide enough efficiency comparable to that of current energy conversion systems. In addition, popular thermoelectric materials containing tellurium and bismuth are toxic and hazardous. These have been barriers that impeded wide use of thermoelectric systems. Despite tremendous amount of effort, significant progresses have not been made in thermoelectric materials over the last 40 years after the discovery of bismuth telluride alloys.[1]

A measure of the efficiency of a thermoelectric material can be described by the thermoelectric figure of merit (often called as *ZT*), which is defined as $S^2\sigma T/k$, where S, σ, T, and k are thermopower (or Seebeck coefficient), electrical conductivity, temperature, and thermal conductivity, respectively. In order to achieve high *ZT*, it is necessary to obtain a large $S^2\sigma$ (called as a power factor) but a small k. The three properties, however, are strongly correlated—changing one parameter favorably often makes the others undesirable. One possible way of avoiding this strong interdependence is to suppress phonon transport without disturbing electron transport significantly as thermal conductivity (k) is composed of phonon and electron parts. Recently, this approach was demonstrated to be beneficial for improving *ZT* of the materials synthesized by mixing different elements or modifying the crystal structures of the current state-of-the-art thermoelectric alloys composed of bismuth, antimony, tellurium, and selenium. These materials such as Bi_2Te_3/Sb_2Te_3 superlattices,[2] PbSeTe/PbTe superlattices,[3] and $AgPb_{18}SbTe_{20}$ nanodots[4] contain many interfaces or inclusions that influence phonon transport rather than electron, which would result in larger suppression in thermal conductivity than electrical conductivity. These interfaces and inclusions have been found to be an effective way of suppressing heat transport by phonons in other materials as well.[5,6]

It might therefore be possible to obtain a huge increase in *ZT* if we modify the phonon transport in a material with an excellent power factor but a moderate-to-high thermal conductivity. Note that the previously reported *ZT* enhancement has been obtained from altering bismuth telluride alloys whose thermal conductivity is small, ~1 W/m K at 300 K. In this regard, complex oxides are best suited to this purpose. In general, their thermopowers are often large due to strong electron correlation[7] and their electrical conductivity can be dramatically tuned by using various doping methods. For example, the power factor of $NaCo_2O_4$ has been reported to be larger than that of the bismuth telluride alloy due to a moderate thermopower (~0.1 mV/K at ~300 K) even with a metal-like electrical conductivity ($\sim 5\times 10^5\ \Omega^{-1}\,m^{-1}$ at ~300 K), but its thermal conductivity has been found to be higher than that of bismuth telluride alloys.[8,9] Another example is strontium titanate, in which electrical conductivity can be dramatically changed from zero to metal-like $\sim 10^6\ \Omega^{-1}\,m^{-1}$ at room temperature by doping various elements including lanthanum, yttrium, and niobium.[10–14] In addition, a large thermopower up to ~890 μV/K at room temperature can be obtained when $SrTiO_3$ is oxygen deficient.[14,15] Nevertheless, their *ZT*'s are not competitive due to their moderate thermal conductivity, ~11 W/m K at 300 K. In this paper, we suggest possible pathways of suppressing the thermal conductivity of complex oxides through incorporating vacancies and defects. The following describe material synthesis processes, measurement methods, and experimental results.

Pulsed laser deposition has been used to epitaxially grow $Sr_{1-x}La_xTiO_{3-\delta}$ ($\delta>0$) films on ~5 mm × 5 mm × 500 μm $SrTiO_3/Si$ substrates. The $SrTiO_3/Si$ substrate represents a

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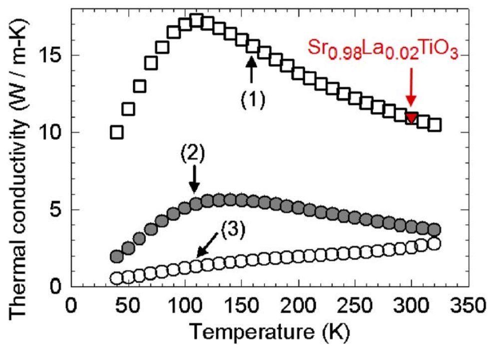

FIG. 1. (Color online) Thermal conductivities of a single-crystal bulk $SrTiO_3$ (□) [indicated by (1)], $Sr_{1-x}La_xTiO_{3-\delta}$ films grown on $SrTiO_3$/Si substrates at 650 °C (●) [indicated by (2)] and 450 °C (○) [indicated by (3)], and a $Sr_{0.98}La_{0.02}TiO_3$ bulk (▼) adopted from Okuda *et al.* (Ref. 10).

silicon substrate with ~10 nm thick molecular-beam epitaxially grown $SrTiO_3$ film. Samples were synthesized under a high vacuum of $\sim 10^{-7}$ Torr throughout the entire process so as to create oxygen vacancies in the film. Two different growth temperatures, 650 and 450 °C, were used and the samples were cooled at ~2.5 °C/min or less. The thicknesses of the films grown at 650 and 450 °C were measured to be 1319 and 562 nm, respectively. The lanthanum concentration x was measured to be ~2% by a Rutherford backscattering method. We used a 3ω method[16] for measuring out-of-plane thermal conductivity of the film in a vacuumed cryostat at a temperature range of 40–320 K. For this method, an ac current was passed through a metal line patterned on a film, and the amplitudes of the first and third harmonic voltage drops along the line were measured for extracting thermal conductivity of the film. Therefore, we had to prevent any parasitic current from flowing through the electrically conducting $Sr_{1-x}La_xTiO_{3-\delta}$ films. Thus, we deposited SiO_2 insulation layers on the samples and reference bare-$SrTiO_3$/Si substrates simultaneously and measured both in order to subtract temperature drops across the electrically nonconducting layer using a differential 3ω scheme.[17] In addition, we prepared a stoichiometric single-crystalline $SrTiO_3$ bulk and patterned a metal line as well for measuring thermal conductivity.

Figure 1 shows out-of-plane thermal conductivities of the $SrTiO_3$ bulk and the $Sr_{1-x}La_xTiO_{3-\delta}$ films. The thermal conductivity of a $Sr_{0.98}La_{0.02}TiO_3$ from Okuda *et al.*[10] has been included for comparison. We observed a large thermal conductivity reduction in the oxygen-deficient samples [indicated by (2) and (3) in Fig. 1] compared to the thermal conductivity of the stoichiometric $SrTiO_3$ [indicated by (1) in Fig. 1] and the $Sr_{0.98}La_{0.02}TiO_3$ (indicated by a triangle in Fig. 1). For example, the room temperature thermal conductivities of $Sr_{1-x}La_xTiO_{3-\delta}$ samples grown at 650 and 450 °C were measured to be ~3.88 and 2.55, respectively, which show ~2.8 and ~4.3 times reduction from the unreduced $SrTiO_3$, respectively. The large reduction could be attributed to effective phonon scattering due to the randomly distributed and clustered nature of oxygen vacancies.[6,18] In addition, the size of the clustered oxygen vacancies, approximately a few nanometers[18] would be comparable to the dominant wavelength of phonons, which could make phonon scattering more efficient.[6,19] At low temperatures, the dominant phonon wavelength could be estimated to be on the order of several nanometers or less from the phonon spectrum, $D(\nu)f_{BE}$, where $D(\nu)$, ν, and f_{BE} are the phonon density of states from the Debye approximation, phonon frequency, and the Bose–Einstein distribution. On the other hand, small atomic La substitutions in $Sr_{0.98}La_{0.02}TiO_3$ appear to have negligible influence on thermal conductivity as the thermal conductivities of both $SrTiO_3$ and $Sr_{0.98}La_{0.02}TiO_3$ are very close. There might be a slight reduction in phonon thermal conductivity from the La doping as the thermal conductivity of electrically conducting $Sr_{0.98}La_{0.02}TiO_3$ includes electronic thermal conductivity, as opposed to the insulating stoichiometric $SrTiO_3$. Nevertheless, the influence of La doping on thermal conductivity would not be significant as the electronic part is estimated to be small, ~0.5 W/m K from the Wiedemann–Franz law.

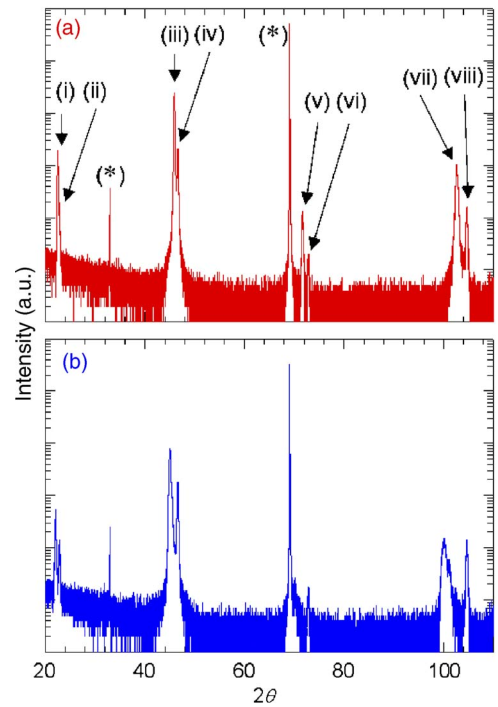

FIG. 2. (Color online) X-ray diffraction of $Sr_{1-x}La_xTiO_{3-\delta}$ grown at (a) 650 °C and (b) 450 °C. $Sr_{1-x}La_xTiO_{3-\delta}$ (100), (200), (300), and (400) peaks are indicated by (i), (iii), (v), and (vii), respectively, and $SrTiO_3$ (100), (200), (300), and (400) peaks are indicated by (ii), (iv), (vi), and (viii), respectively. Two peaks (*) are from Si substrates.

Furthermore, we found that a low-temperature synthesis process at 450 °C yielded even lower thermal conductivity [indicated by (3) in Fig. 1]. While the $SrTiO_3$ and $Sr_{0.98}La_{0.02}TiO_3$ have substitutions or defects that would be smaller than several nanometers, this process could have produced phonon-scattering defects such as dislocations and low-angle grain boundaries—whose characteristic length could be longer than that of the oxygen vacancies—that would be responsible for scattering mid- and/or long-wavelength phonons. The suppression of peak thermal conductivity of the samples indicated by (1) and (2) at 110–120 K would suggest this scattering, as dominant phonon wavelengths at low temperatures would be longer than those of high temperatures. Note that the thermal conductivity reduction would not be related to the corruption of film crystallinity resulting in amorphous or polycrystalline microstructures, as indicated by typical x-ray diffraction patterns (Fig. 2). They show highly crystalline single-phase peaks with a narrow full width at half maximum in rocking ($\omega \sim 0.25°$). The intensity peaks for $Sr_{1-x}La_xTiO_{3-\delta}$ grown at 450 °C that appeared at lower 2θ compared to those at 650 °C would indicate a higher concentration of oxygen vacancies,[20,21] and the broader peaks for the sample grown at 450 °C than those of the 650 °C sample would suggest higher defect concentration. Finally, the large reduction in thermal conductivity from oxygen vacancies could be very beneficial in enhancing *ZT* of strontium titanates—possibly many oxygen-contained complex oxides—as the absence of oxygen in the crystal lattice provides free electrons and alters electron density of states[15,22] that often give rise to an increase of electrical conductivity and a large thermopower. Considering that *ZT* of $Sr_{0.98}La_{0.02}TiO_3$ is ~0.1 at ~300 K,[10] we could estimate $ZT \sim 0.4$ from the thermal conductivity reduction for oxygen-deficient one under the assumption that the power factor of $Sr_{0.98}La_{0.02}TiO_3$ does not change significantly. It might be also possible to reduce the thermal conductivity down to a value close to the electronic thermal conductivity of ~0.5 W/m K at ~300 K by incorporating other phonon suppression methods such as embedding various size nanostructures, which have been proven to be effective to deplete phonon thermal conductivity.

In summary, we report a significant thermal conductivity reduction in oxygen-deficient La-doped strontium titanate ($Sr_{1-x}La_xTiO_{3-\delta}$) films, as compared to unreduced strontium titanates such as $SrTiO_3$ and $Sr_{0.98}La_{0.02}TiO_3$ bulks. Our experimental results suggest that oxygen vacancies and defects from film growth processes in oxygen-deficient low-temperature environment could provide strong phonon scattering, resulting in large thermal conductivity suppression. This outcome could be very useful for the design of better thermoelectric materials, particularly in complex oxides as they have been overlooked for high-efficiency thermoelectrics due to their moderate thermal conductivity despite excellent electrical properties for thermoelectrics.

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