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Cite as: J. Appl. Phys. 117, 075101 (2015); https://doi.org/10.1063/1.4908209
Submitted: 27 November 2014. Accepted: 03 February 2015. Published Online: 18 February 2015

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Reduced thermal conductivity by nanoscale intergrowths in perovskite like layered structure La$_2$Ti$_2$O$_7$

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(Received 27 November 2014; accepted 3 February 2015; published online 18 February 2015)

The effect of substitution and oxidation-reduction on the thermal conductivity of perovskite-like layered structure (PLS) ceramics was investigated in relation to mass contrast and non-stoichiometry. Sr (acceptor) was substituted on the A site, while Ta (donor) was substituted on the B site of La$_2$Ti$_2$O$_7$. Substitution in PLS materials creates atomic scale disorders to accommodate the non-stoichiometry. High resolution transmission electron microscopy and X-ray diffraction revealed that acceptor substitution in La$_2$Ti$_2$O$_7$ produced nanoscale intergrowths of n = 5 layered phase, while donor substitution produced nanoscale intergrowths of n = 3 layered phase. As a result of these nanoscale intergrowths, the thermal conductivity value reduced by as much as ~20%. Pure La$_2$Ti$_2$O$_7$ has a thermal conductivity value of ~1.3 W/m K which dropped to a value of ~1.12 W/m K for Sr doped La$_2$Ti$_2$O$_7$ and ~0.93 W/m K for Ta doped La$_2$Ti$_2$O$_7$ at 573 K. © 2015 AIP Publishing LLC.

[http://dx.doi.org/10.1063/1.4908209]

INTRODUCTION

Thermoelectrics can convert waste heat into electricity by utilizing the Seebeck effect.$^1$ They do not possess any moving parts, which make them potentially reliable and long lasting.$^2$ The efficiency of a thermoelectric material can be represented by a dimensionless figure of merit (zT) which depends on Seebeck coefficient (S), electrical conductivity (σ), and thermal conductivity (κ). Conventional thermoelectric materials, like Bi$_2$Te$_3$, skutterudites, and PbTe are classed as efficient thermoelectric materials. Bi$_2$Te$_3$ related compounds have a maximum efficiency near room temperature ($<$200 °C), while skutterudites and PbTe are classed as intermediate temperature thermoelectrics (up to 650 °C).$^4$–$^8$ These materials are being used in large scale applications but they have high processing costs$^9$ and use toxic elements. Most of these materials have zT close to unity, but they are not stable in air due to the oxidation at these temperatures.$^{10}$

Oxide materials are inexpensive, abundant in nature, non-toxic, and environmentally friendly. These materials possess high chemical and thermal stability which makes them suitable for high temperature thermoelectric application in air.$^{11,12}$ Oxide materials offer great flexibility in structural and compositional variations to alter their thermoelectric properties. Na$_x$Co$_2$O$_4$ based oxides have shown some promising results,$^{13}$ but toxicity of cobalt and volatility of Na are a concern.$^*$

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possibility of inducing disorder.\textsuperscript{24} By engineering the microstructure of the layered compounds, the thermal conductivity can be reduced by creating more scattering centres.\textsuperscript{25} In this work, we substituted Sr and Ta in La$_2$Ti$_2$O$_7$ to create defects inside the microstructure due to mismatch between valence, atomic radii and the atomic weights of the host and the substituted elements.

The objective of this work is to investigate for the first time, the effect of acceptor-donor substitution and oxidation-reduction on the thermal conductivity due to atomic scale defects in La$_2$Ti$_2$O$_7$.

**EXPERIMENTAL PROCEDURE**

La$_2$Ti$_2$O$_7$, La$_{1.6}$Sr$_{0.4}$Ti$_2$O$_{6.8}$, and La$_2$Ti$_{1.7}$Ta$_{0.3}$O$_{7.15}$ were prepared by solid state reaction. The starting materials were La$_2$O$_3$ (99.99% purity, Sigma Aldrich), SrCO$_3$ (99.9% purity, Sigma Aldrich), TiO$_2$ (anatase) (99.6% purity, Alfa aesar), and Ta$_2$O$_5$ (99.85% purity, Alfa aesar). These powders were mixed in stoichiometric ratios and ball milled using ethanol as a milling medium in a planetary ball mill. Mixed powders were calcined at 1300°C for 4 h. After calcination, the powders were remilled for 4 h to break the agglomerates and reduce the particle size.

Calcined powders were sintered using a Spark Plasma Sintering (SPS) furnace (HPD 25/1, FCT, Rauenstein, Germany). The powders were cold pressed into a 20 mm graphite die and sintered at 1350°C under 50 MPa of pressure for 5 min. The vacuum level inside the furnace was ~5 Pa. The sintered discs were annealed at 1000°C for 6 h to remove any carbon contamination. For comparison, the air annealed discs were reduced at 1200°C for 4 h in a mixture of 10% H$_2$ and 90% Ar in a laboratory furnace (thermal technology LLC, Model number 1100 2560 1/2). The bulk density was measured by Archimedes principle and presented in Table I. All sintered samples were more than 98% dense.

**SAMPLE CHARACTERIZATION**

X ray diffraction (XRD) patterns for powders, as sintered, air annealed, and hydrogen reduced samples were obtained using an X-ray diffractometer (Siemens D5000, Karlsruhe, Germany) using CuK$_\alpha$ radiation. The microstructures of the ceramic samples were observed using Transmission Electron Microscopy (TEM) Jeol JEM 2010 200KV. All of the ceramics were observed along the pressing direction. The samples for TEM were prepared using a Precision Ion polishing System (PIPS$^\text{TM}$). Thermal conductivity was calculated using the formula $\kappa = \rho C_p D$, where $\rho$ is the density measured by Archimedes principle, $C_p$ is the specific heat measured using a Netzsch STA (449 F3 Jupiter), and $D$ is the thermal diffusivity measured using a netszch LFA 457 microflash using 20 mm discs under Ar environment. The thermal diffusivity measurements were repeated to check reproducibility of the measurement. Elastic modulus was measured by Micro Indentation Tester from CSM Instruments (Switzerland) with a 100 μm radius spherical diamond indenter tip. The valence of the elements was determined by the X-ray photoelectron spectroscopy (XPS; ESCALAB MK II, VG Scientific). All the spectra are corrected against the C reference peak at 285 eV for different elements.

**RESULTS AND DISCUSSIONS**

The La$_2$Ti$_2$O$_7$ was single phase after calcination, sintering, and subsequent heat treatments. The XRD peaks matched the PDF card # 28-0517 (supplementary material).\textsuperscript{26} Figure 1(a) shows the X-ray diffraction patterns for La$_{1.6}$Sr$_{0.4}$Ti$_3$O$_{8.8}$, and most of the grains were defect free except for a few planar defects. Figure 2(b) shows a typical bright field TEM image of the La$_2$Ti$_2$O$_7$ based ceramics after air annealing. The typical grain size was ~0.7 μm and most of the grains were defect free except for a few planar defects. Figure 2(b) shows a typical bright field TEM image of the La$_2$Ti$_2$O$_7$ based ceramics after air annealing. The typical grain size was ~0.7 μm and most of the grains were defect free except for a few planar defects. Figure 2(b) shows a typical bright field TEM image of the La$_2$Ti$_2$O$_7$ based ceramics after air annealing.

**TABLE I. Archimede’s density for La$_2$Ti$_2$O$_7$ based ceramics.**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Density, g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$_2$Ti$_2$O$_7$, air annealed</td>
<td>5.74 ± 0.04</td>
</tr>
<tr>
<td>La$_2$Ti$_2$O$_7$, reduced</td>
<td>5.62 ± 0.01</td>
</tr>
<tr>
<td>La$<em>{1.6}$Sr$</em>{0.4}$Ti$<em>3$O$</em>{8.8}$, air annealed</td>
<td>5.53 ± 0.03</td>
</tr>
<tr>
<td>La$<em>{1.6}$Sr$</em>{0.4}$Ti$<em>3$O$</em>{8.8}$, reduced</td>
<td>5.47 ± 0.01</td>
</tr>
<tr>
<td>La$<em>2$Ti$</em>{1.7}$Ta$<em>{0.3}$O$</em>{7.15}$, air annealed</td>
<td>6.07 ± 0.02</td>
</tr>
<tr>
<td>La$<em>2$Ti$</em>{1.7}$Ta$<em>{0.3}$O$</em>{7.15}$, reduced</td>
<td>5.98 ± 0.03</td>
</tr>
</tbody>
</table>
TABLE II. Mass percentage of the secondary phase in Sr and Ta substituted La$_2$Ti$_2$O$_7$.

<table>
<thead>
<tr>
<th>Powder (mass %)</th>
<th>Sinter (mass %)</th>
<th>Air Annealed (mass %)</th>
<th>Reduced (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{1.6}$Sr$</em>{0.4}$Ti$<em>2$O$</em>{6.5}$</td>
<td>...</td>
<td>8.4</td>
<td>3.0</td>
</tr>
<tr>
<td>La$<em>2$Ti$<em>1.7$Ta$</em>{0.3}$O$</em>{7.15}$</td>
<td>3.6</td>
<td>4.6</td>
<td>4.6</td>
</tr>
</tbody>
</table>

FIG. 1. XRD patterns of (a) La$_{1.6}$Sr$_{0.4}$Ti$_2$O$_{6.5}$ and (b) La$_2$Ti$_1.7$Ta$_{0.3}$O$_{7.15}$.

FIG. 2. TEM images of (a) air annealed La$_2$Ti$_2$O$_7$; (b) lattice image of air annealed La$_2$Ti$_2$O$_7$; (c) air annealed La$_{1.6}$Sr$_{0.4}$Ti$_2$O$_{6.5}$; (d) lattice image of air annealed La$_{1.6}$Sr$_{0.4}$Ti$_2$O$_{6.5}$; (e) air annealed La$_2$Ti$_1.7$Ta$_{0.3}$O$_{7.15}$, and (f) lattice image of air annealed La$_2$Ti$_1.7$Ta$_{0.3}$O$_{7.15}$.
intergrowths had a (100)₅ || (100)₄ epitaxy and were distributed homogeneously throughout the ceramic. Some of the intergrowths terminated or moved to a different plane of the La₂Ti₂O₇ as shown in Figure 2(d). When an intergrowth terminated, it disturbed the neighbouring planes as seen in Figures 2(c) and 2(d).

Figure 2(e) shows a bright filed TEM image of La₂Ti₁.₇Ta₀.₃O₇.₁₅ ceramic after air annealing with some planar defects which were distributed homogeneously throughout the ceramic. From XRD data, the formation of three layered perovskite phase was confirmed. So, the regions of planar defects are the regions of three layered perovskite phase embedded inside four layered La₂Ti₂O₇. The morphology of the intergrowths in La₂Ti₁.₇Ta₀.₃O₇.₁₅ is different from that in La₁.₆Sr₀.₄Ti₂O₆.₈. These intergrowths are shorter and terminate within the 4 layer PLS phase as shown in the inset in Figure 2(f).

Figures 3(a)–3(c) show the XPS spectra of surface electrons for different elements in La₂Ti₂O₇ ceramics after ion beam etching. The ion beam etching was done for 5 min. Since the C reference used by different labs varies, the absolute value of each element varies in a range. The binding energy (BE) values for La 3d showed a clear doublet for both components (La₃d₅/₂ and La₃d₃/₂) which is a characteristic of La containing oxide compounds. The binding energy difference between the splitting of La₃d₅/₂ and La₃d₃/₂ was ~4.6 eV and ~4.4 eV, respectively, for all of the ceramics. The BE values for Ti 2p showed a clear doublet (Ti 2p₁/₃ and Ti 2p₃/₂). For air annealed La₂Ti₂O₇, the peak position is marked as A (459.17 eV) and the full width half maximum (FWHM) matches the Ti⁴⁺ state. The Ti 2p₃/₂ peak is slightly asymmetric and it gives rise to another peak at 457.67 eV which is marked as B. This peak was caused by the presence of Ti³⁺ state. After reduction, one additional
peak can be seen at 453.9 eV which is marked as C. This peak can be attributed to the Ti$^{2+}$ state as reported in the literature. The intensity of the peak marked as B also increased in the reduced ceramic. The B peak which was observed for Ti 2p in pure La$_2$Ti$_2$O$_7$ had very low intensity after Ta substitution. All of the O 1s spectra show the same peak symmetry towards the lower binding energy side which can be attributed to the bonded oxygen in the structure as reported in literature. The small higher binding energy peak indicates chemisorbed oxygen or absorbed hydroxyl ions. The FWHMs of the O 1s peak are given in Table III for all the compositions. The FWHM for air annealed La$_2$Ti$_2$O$_7$ was 1.48 which decreased to 1.36 after reduction. Sr and Ta substituted La$_2$Ti$_2$O$_7$ gave interesting results; the FWHM for O 1s of La$_{1.6}$Sr$_{0.4}$Ti$_2$O$_{6.8}$ and La$_2$Ti$_{1.7}$Ta$_{0.3}$O$_{7.15}$ were 1.38 and 1.51, respectively. This change in FWHM supports the fact that the Sr and Ta substitution in La$_2$Ti$_2$O$_7$ produced nanoscale intergrowths (five layer and three layer PLS compounds, respectively) which have different oxygen to cation ratio compared to La$_2$Ti$_2$O$_7$ (A:B:O is 1:1:3.5 for La$_2$Ti$_2$O$_7$, A:B:O is 1:1:3.4 for A$_2$B$_3$O$_{11}$, and 1:1:3.7 for A$_3$B$_3$O$_{11}$).

In order to improve the quantitative analysis of the XPS data, the binding energy difference ($\Delta E$) method was used to reduce scatter in the data and to enable better comparison with the literature. $\Delta E$ for the pure and Sr/Ta substituted La$_2$Ti$_2$O$_{7.25}$, is given in Table III. The $\Delta E$ for Ti-O for air annealed and hydrogen reduced La$_2$Ti$_2$O$_{7.25}$ samples was calculated to be 71.5 eV and 71.6 eV, respectively. These values are in good agreement with the published literature. The $\Delta E$ for La-O for air annealed La$_2$Ti$_2$O$_7$ was found to be 304.7 eV which decreased to 304.2 eV after reduction. This decrease in binding energy was due to a decrease in bonding strength as a result of oxygen removal after reduction. The $\Delta E$ for Ti-O did not change after the addition of Sr. After Sr substitution, the $\Delta E$ for La-O was 304.4 eV which was lower than the pure air annealed La$_2$Ti$_2$O$_7$ but higher than the pure reduced La$_2$Ti$_2$O$_{7.25}$. Since La-O bonds are weaker than Ti-O bonds (bond strengths are reported in Ref. 39), the $\Delta E$ results for La-O and Ti-O bonds suggest the presence of localised planar defects/intergrowths in the reduced and Sr substituted La$_2$Ti$_2$O$_7$ caused further weakening of the La-O bonds. This also proves the stability of Ti-O bonds in the PLS compounds as a result of substitution/heat treatment. $\Delta E$ for Sr-O was calculated to be 397 eV and it agrees with the reported value.

Based on the microstructural characterization of partially substituted La$_2$Ti$_2$O$_7$, it is interesting to study the effect of nanoscale intergrowths on the thermal conductivity. Figure 4(a) shows the thermal conductivity of air annealed La$_2$Ti$_2$O$_7$ based ceramics. The thermal conductivity of La$_2$Ti$_2$O$_7$ is nearly temperature independent as reported in the literature for similar PLS compounds (Sr$_2$Nb$_2$O$_7$). The thermal conductivity for La$_2$Ti$_2$O$_7$ was ~1.3 W/m K in this work, which was close to that of other layered structured compounds, e.g., Bi$_3$Ti$_2$O$_7$ (~1 W/m K). After Sr substitution, the thermal conductivity increased with increasing temperature. The thermal conductivity of La$_2$Ti$_{1.7}$Ta$_{0.3}$O$_{7.15}$ ceramics is nearly temperature independent like La$_2$Ti$_2$O$_7$ and decreased with Ta substitution. Figure 4(b) shows the thermal conductivity of reduced La$_2$Ti$_2$O$_7$ based ceramics. After reduction, the values of thermal conductivity for La$_2$Ti$_{1.7}$Ta$_{0.3}$ and La$_{1.6}$Sr$_{0.4}$Ti$_2$O$_{6.8}$ ceramic decreased as compared to the corresponding air annealed sample and the value was less temperature dependent. This decrease in thermal conductivity was caused by the increased amount of nanoscale intergrowths inside the structure as indicated by the TEM and XRD (Table II). While in the case of La$_2$Ti$_{1.7}$

![FIG. 4. Variation in thermal conductivity of pure and substituted La$_2$Ti$_2$O$_7$ (a) air annealed and (b) reduced.](image-url)
Ta_{0.3}O_{7.15±0.5}, the value of thermal conductivity decreased only slightly compared to the corresponding air annealed sample.

In order to study the effect of compositional non-stoichiometry on the thermal conductivity, the electronic contribution of thermal conductivity was calculated using the Wiedemann–Franz law to separate its contribution from the lattice thermal conductivity. The Wiedemann–Franz law is given by

$$k_{elec} = LT\sigma,$$

(1)

where $k_{elec}$ is the electronic contribution of thermal conductivity, $L$ is the Lorenz number, $T$ is the absolute temperature, and $\sigma$ is the electrical conductivity. The value of $L$ was taken from literature as $2.44 \times 10^{-8}$ W $\Omega$ K$^{-2}$ at 573 K.\(^{42}\) Electrical conductivity was measured using the four probe method in vacuum with laboratory built equipment\(^{43}\) and was estimated to be $\sim 0.5$ S/m for La$_{1.6}$Sr$_{0.4}$Ti$_2$O$_{6.8±0.5}$. This had the highest electrical conductivity measured for the substituted PLS ceramics in this work. Based on these values, the $k_{elec}$ for La$_2$Ti$_2$O$_7$ based compositions was estimated to be $<7 \times 10^{-9}$ W/m K, which is very low and it can be concluded that the changes in thermal conductivity were mainly due to the changes in lattice thermal conductivity.\(^{44}\)

There are potentially two main mechanisms that could influence the thermal conductivity of La$_2$Ti$_2$O$_7$ in the present study, mass contrast, and the effect of the nanoscale intergrowths generated as the result of substitution. The effect of change in atomic mass on the thermal conductivity is given by the expression\(^{45}\)

$$\kappa_{min} = 0.87k_B\Omega^{2/3}\left(\frac{E}{\rho}\right)^{1/2},$$

(2)

where $E$ is the elastic modulus, $\rho$ is the density, and $\Omega$ is the average atomic volume. $k_B$ is the Boltzmann’s constant. The estimated minimum thermal conductivity values are presented in Table IV.

The average atomic volume for La$_2$Ti$_2$O$_7$ based compositions was calculated using the following relation and tabulated in Table IV (Ref. 46)

$$\Omega = \frac{M}{m\rho N_A},$$

(3)

where $M$ is the average molar mass of the unit cell, $m$ is the number of atoms per formula unit, $\rho$ is the density, and $N_A$ is the Avogadro’s number.

From the above two expressions, it is evident that large mean atomic mass and low elastic modulus favour low thermal conductivity. The atomic masses of La$_2$Ti$_2$O$_7$ based compositions are given in Table IV. It is evident from the Table IV that after substitution the atomic mass decreases in the case of La$_{1.6}$Sr$_{0.4}$Ti$_2$O$_{6.8±0.5}$ and increases in the case of La$_2$Ti$_{1.7}$Ta$_{0.3}$O$_{7.15±0.5}$ compared to pure La$_2$Ti$_2$O$_7$. After substituting the elastic modulus (E), the thermal conductivity will increase slightly in the case of La$_{1.6}$Sr$_{0.4}$Ti$_2$O$_{6.8±0.5}$ and decrease in the case of La$_2$Ti$_{1.7}$Ta$_{0.3}$O$_{7.15±0.5}$. These values hold true for the defect free crystals, but in the case of substituted La$_2$Ti$_2$O$_7$, a high density of nanoscale intergrowths was found in the microstructure. Therefore, the thermal conductivity depends on both, the atomic mass difference and the nanoscale intergrowths. This would explain why the experimental thermal conductivities were lower than the minimum theoretical thermal conductivities. This decrease in thermal conductivity by substituting different elements can be explained by the fact that substituted elements produce nanoscale intergrowths in the structure to accommodate non-stoichiometry. The phonons are scattered by these nanoscale intergrowths, thus reducing the thermal conductivity compared to the pure compound (and theoretical minimum thermal conductivity values).

In order to estimate the effect of nanoscale intergrowths/secondary phase on thermal conductivity, the difference between the theoretical thermal conductivity (given in Table IV) and the experimental thermal conductivity was calculated. This difference was negligible in the case of the pure compound. However, the difference increased up to $\sim 20\%$ in the substituted compositions.

**CONCLUSION**

The effect of acceptor/donor substitution and oxidation-reduction was studied on La$_2$Ti$_2$O$_7$. High resolution TEM and XRD revealed that acceptor doping of La$_2$Ti$_2$O$_7$ produced nanoscale intergrowth regions of $n=5$ layered phase inside $n=4$ layered phase, while donor doping produced nanoscale intergrowth regions of $n=3$ layered structure. Reduction increased the density of nanoscale intergrowths in Sr substituted La$_2$Ti$_2$O$_7$, while it decreased them in Ta substituted La$_2$Ti$_2$O$_7$. These nanoscale intergrowths and mass contrast affected the thermal conductivity of substituted La$_2$Ti$_2$O$_7$. The thermal conductivity decreased with the increasing amount of nanoscale intergrowths that were generated to accommodate compositional non-stoichiometry. A $\sim 20\%$ decrease in the thermal conductivity was achieved due to the nanoscale intergrowths. A very low thermal conductivity value of $\sim 0.93$ W/m K was observed in Ta substituted La$_2$Ti$_2$O$_7$ at 573 K. These results suggest that nanoscale intergrowths can effectively reduce the thermal...
conductivity of layered perovskites and thus improve their thermoelectric properties. This approach can also be applied to other layered perovskite compounds. For example, the deviation in stoichiometry produced by the substitution of Sr by other layered perovskite compounds. For example, the thermoelectric properties. This approach can also be applied to the formation of nanoscale intergrowths of layered perovskites.

ACKNOWLEDGMENTS

The authors would like to thank Dr. Na Ni of Imperial College of London, UK and Mr. Samuel Jackson of University of Manchester, UK.