Anisotropy of Lattice Thermal Conduction in TiO_{2-x} with High Density of Planar Defects by Atomistic Simulations

Y. Miyauchi[1], M. Tada[1], M. Yoshiya[1, 2], S. Harada[3], K. Tanaka[4], H. Yasuda[1], H. Inui[5]

[1]Department of Adaptive Machine Systems, Osaka University, Osaka, 565-0871, Japan
[2]Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya, 456-8587, Japan
[3]Department of Materials, Physics and Energy Engineering, Nagoya University, Nagoya 464-8603, Japan
[4]Department of Mechanical Engineering, Kobe University, Kobe, 657-8501, Japan
[5]Department of Materials Science and Engineering, Kyoto University, Kyoto, 606-8501, Japan

Titanium oxides are widely used for catalytic, pigment and electrical materials owing properties originating from their various structures and compositions. TiO_2 exists in a number of polymorphs: rutile, anatase and brookite. Ti_2O_3 has the corundum structure. In particular Magnéli phase Ti_nO_{2n-1} (n=3, 4 …) has attracted greater attention as a thermoelectric material. Magnéli phase is synthesized by reduction of rutile under controlled Po_2, and possesses crystallographic shear planes. The shear planes are periodically positioned and their separations are as small as several ångströms depending n. This structure consists of rutile layers sandwiching Ti_2O_3 layers at the shear planes. A larger n indicates a thicker rutile layer. It is well known that electronic conductivity of Ti_nO_{2n-1} is metallic at room temperature [1], originating from d^1 configuration of Ti^{3+} ions. In contrast, the shear planes scatter phonons, resulting in the decrease in lattice thermal conductivity of Ti_nO_{2n-1} [2]. Although the decrease in the lattice thermal conductivity is significant, being advantageous for the enhancement of thermoelectric figure of merit, our understanding of the mechanism behind the low thermal conductivity in Ti_nO_{2n-1} is still limited since conventional theories of thermal conduction for metals and semiconductors are not directly applicable to metal oxides.

In this study, in order to acquire strategies to improve the thermoelectric properties of Ti_nO_{2n-1}, theoretical calculations of lattice thermal conductivity were performed to elucidate the more detailed mechanism behind low lattice thermal conductivity in Ti_nO_{2n-1}. Thermal conduction in TiO_{2-x} (x=0~0.5) including Magnéli phase has been analyzed by the perturbed molecular dynamics calculation [3]. In this method, contributions of each constituent element for lattice thermal conductivity can be quantitatively analyzed. We used the empirical interatomic potential function and its parameters [4] which reproduce lattice constants, thermal expansion coefficients and elastic constants of rutile, anatase and Ti_2O_3.

Lattice thermal conductivities of several TiO_{2-x} models have been calculated. First of all, lattice thermal conductivity decreased with an increase in temperature in accordance with phonon-phonon scattering mechanism. In addition lattice thermal conductivity along a-axis was lower than that along c-axis in rutile. These tendencies satisfactorily agree with the experimental results by Charvat et al. [5]. In anatase, lattice thermal conductivity along c-axis is lower than that along a-axis due to a smaller contribution of O. On the other hand, in Magnéli phase Ti_4O_7, as shown in Fig. 1, lattice thermal conductivity was significantly suppressed compared with those of bulk rutile and Ti_2O_3 owing to the presence of the planar defects in their crystal structures. This result can be explained by the increased phonon scattering due to distorted atomic

configuration in the vicinity of the shear planes. Lattice thermal conductivity along and across the shear planes of Ti_nO_{2n-1} (n=7~9) at 300 K are shown in Fig. 2. A smaller n indicates a higher density of planar defects. As seen from Fig. 2, lattice thermal conductivity decreased as the separation of shear planes decreased. Furthermore, in contrast to intuition based on macroscopic understanding, we found that lattice thermal conductivity along the shear planes is lower than that across the shear planes, which is beneficial for thermoelectric applications due to anisotropy of the electronic conductivity [1]. An additional detailed analysis revealed that the low lattice thermal conductivity along the shear planes can be attributed to larger disorder of coordination environment along the shear planes than that of across the shear planes. This result indicates that a single crystal or a polycrystalline Magnéli phase controlling the planar defects is effective for improving thermoelectric properties.

References

[1] R. F. Bartholomew et al., *Phys. Rev.*, **187** (1969) 828.
[2] S. Harada et al., *J. Appl. Phys.*, **108** (2010) 083703.
[3] M. Yoshiya et al., *Mol. Simulat.*, **30** (2004) 953.
[4] S. Kerisit et al., *J. Phys. Chem. C*, **112** (2008) 7678.
[5] F. R. Charvat et al., *J. Am. Ceram. Soc.*, **40** (1957) 306.

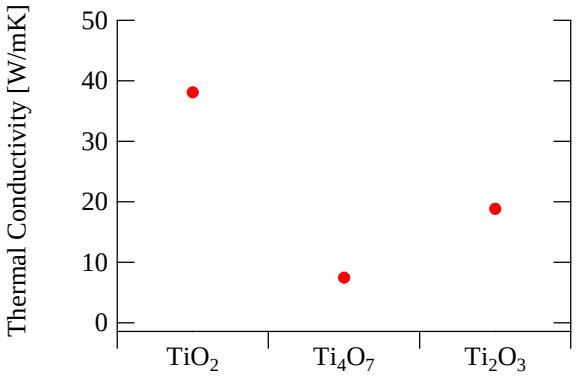

FIG. 1. Lattice thermal conductivity of rutile, Magnéli phase Ti_4O_7 and Ti_2O_3 at 300 K.

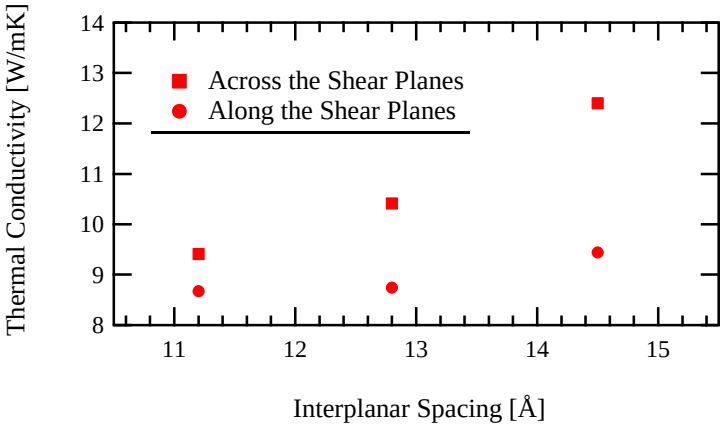

FIG. 2. Lattice thermal conductivity of Ti_nO_{2n-1} (n=7~9, from left to right) at 300 K.