Suppression of Thermal Conduction without Deteriorating Electronic Properties of Magnéli Phase Titanium Oxides by Doping Impurities

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Magnéli phases Ti_nO_{2n-1} (n=3, 4 …) [1], a candidate for n-type thermoelectric materials, contains nanometer-spaced periodic planer defects called shear planes [2] and looks like TiO_2 / Ti_2O_3 layered structure. Larger n of Ti_nO_{2n-1} indicates thicker TiO_2 layers while thickness of Ti_2O_3 layer remain unchanged as Fig. 1 shows atomic coordination in Ti_5O_9. Thermoelectric energy conversion efficiency is quantified by the dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$, where Z, S, σ, T, and κ are the figure of merit, Seebeck coefficient, electrical conductivity, temperature, and thermal conductivity, respectively. It is well known that high electrical conductivity does not decrease even if the shear planes are introduced but rather increases [3], and phonon scattering by those planar defect reduces lattice thermal conductivity of Ti_nO_{2n-1} [4]. Miyauchi et al reported that TiO_2 layers contribute to overall lattice thermal conductivity much more than Ti_2O_3 layers [5] and TiO_2 layers are not responsible for electronic properties. Thus, decreasing local thermal conductivity of TiO_2 layer is one promising way to improve the heat-to-energy conversion efficiency. To realize it, doping impurities selectively into the TiO_2 layer would be effective to suppress overall thermal conductivity without compromising electronic properties governed by Ti_2O_3 layer thereby improving thermoelectric figure of merit of Ti_nO_{2n-1} (Fig. 2).

In this study, attempts have been made to find candidates of doping elements that would not segregate to Ti_2O_3 layer but stay in the TiO_2 layer of Magnéli phase Ti_nO_{2n-1}. To do so, at first, total energies of the bulk structures, rutile phase TiO_2 and corundum phase Ti_2O_3, were calculated by ab initio calculations with the generalized gradient correction approximation for exchange correlation formulated by Perdew, Burke, and Ernzerhof, in order to compare energies required for substitution taking into account other defect species, such as vacancies, interstitials, and extra electrons or holes, to maintain charge neutrality. Then, total energies for impurity-substituted (together with charge-compensating defects) Magnéli phase Ti_5O_9 was carried out by changing position of the defect complex from Ti_2O_3 layer to TiO_2 layer. Influence of the defect complex on electronic properties of Ti_2O_3 layer was analyzed by examining the modification of charge density in the layer. After good candidates to suppress local thermal conductivity of TiO_2 layer without deteriorating electronic structure of Ti_2O_3 layer is found, lattice thermal conductivity of impurity-doped Ti_5O_9 was calculated by the perturbed molecular dynamics [6].

It is found that tetravalent elements, such as Zr, and the combination of pentavalent and trivalent elements, such as Nb and Sc, in particular can be easier to dissolve into bulk TiO_2, in good agreements with earlier studies [7,8]. Total energy calculations of impurity-doped Ti_5O_9 showed that tetravalent elements and combination of pentavalent and trivalent elements stay in the TiO_2 layer instead of segregating to Ti_2O_3 layer. These results indicate that tetravalent elements and the combination of

pentavalent and trivalent elements tend to stay not only in bulk TiO_2 phase but also in TiO_2 layer of Magnéli phase Ti_nO_{2n-1}. Analyses of charge density suggest that doping impurities into TiO_2 layer does not accompany any noticeable change in electronic state of the Ti_2O_3 layer. Furthermore, we found that the lattice thermal conductivity of not only out-of-plane direction but also in-plane direction of impurity-doped Ti_5O_9 is significantly suppressed compared with that of pure Magnéli phase Ti_5O_9. These attempts demonstrated that doping those elements selectively improves its thermoelectric properties through suppressing thermal conductivity without deteriorating electronic properties.

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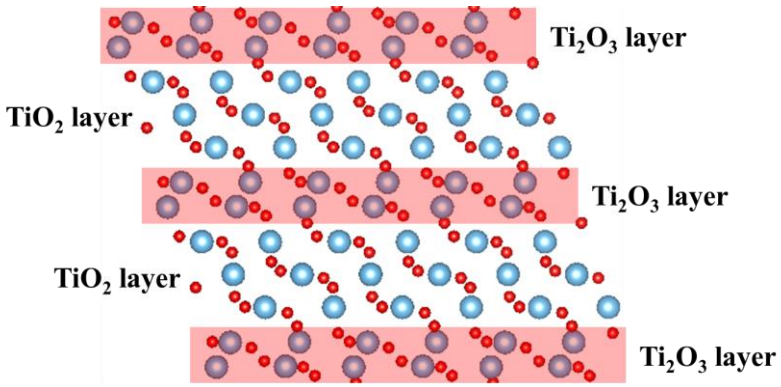

FIG. 1 The crystal structure of Magnéli phase Ti_5O_9

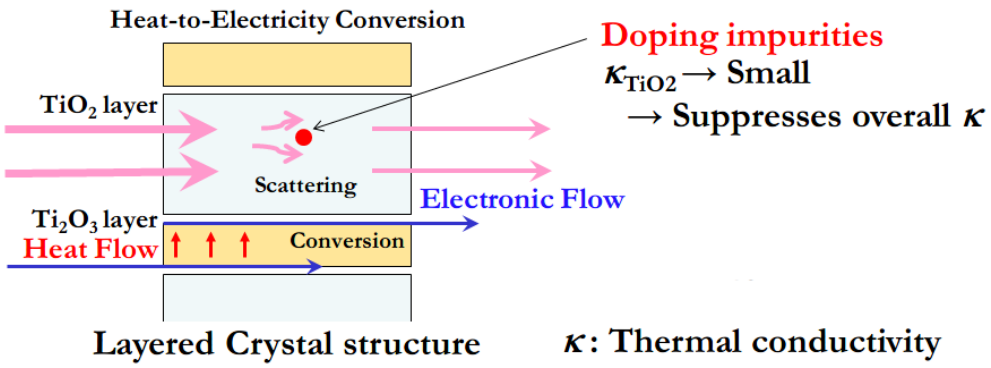

FIG. 2 Schematics of expected impurity doping effects into Magnéli phase Ti_nO_{2n-1}