

論文の内容の要旨

Theoretical prediction of the phase transition route from β to λ phases of trititanium pentoxide
(五酸化三チタンにおける β から λ 相への相転移の理論予測)

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Introduction

Five phases of trititanium pentoxide Ti_3O_5 , α , β , γ , δ and λ are reported up to now. Three of these five phases, α , λ and β phases have pseudobrookite-related structure, and λ and β - Ti_3O_5 have structural phase transition by kinds of external stimulation such as photo-inducing, temperature and pressure [1, 2]. It might be regarded that there is an arrangement of atomic coordination in four of eight inequivalent sites, Ti(3), O(3), O(4) and O(5) in the phase transition (Figure 1.) However, dynamical analysis for the atomic displacement in the phase transition has not been reported yet. This thesis reports about the prediction of the new route of phase transition from β - Ti_3O_5 to λ - Ti_3O_5 under uniaxial tensile. Also, the mechanism for the phase transition is discussed, by a standpoint of theoretical calculation.

Phase transition under uniaxial tensile

To evaluate the atomic-scale dynamics of phase transition, molecular dynamics (MD) calculation was employed for this research. MD calculation can be classified into two types, classical one and *ab initio* one, of which difference is that their potential field is constructed of empirical or not. In this research, both types were applied. Classical MD was performed with LAMMPS package, and *ab initio* MD was performed with OpenMX package, respectively. Crystal structure of β - Ti_3O_5 was constructed from the reported values in a previous research [3]. In a classical MD simulation, a supercell with

8000 atoms (1000 chemical formulas of Ti_3O_5) was prepared. To decrease the computational cost, a primitive unit cell with 16 atoms (2 chemical formulas) was applied for *ab initio* MD. The largest difference between β and λ - Ti_3O_5 unit cell is *c*-axis. λ - Ti_3O_5 has 6 % longer *c*-axis than that of β - Ti_3O_5 , implying that uniaxial strain or stress against *c*-axis will strongly contribute to the phase transition. Based on this idea, classical MD of β - Ti_3O_5 by gradually applying uniaxial stress on *c*-axis was performed. Figure 2 shows the dynamics of atoms in the unit cell, and the trend of *c*-axis length during the classical MD calculation. In the calculation, temperature was controlled at 300 K, by isothermal-isobaric (NPT) ensemble. Specific atomic displacements especially Ti(3) and O(5) sites began around 5 GPa of tensile stress (8000 calculational steps,) consequent to the structural phase transition from β - Ti_3O_5 to λ - Ti_3O_5 . There is an assumption that Ti(3) and O(5) sites will largely move in the phase transition from the similarity of these two structures, though this dynamics is not confirmed by experimental nor theoretical way. The atomic displacement was not occurred simultaneously in all part of the supercell, but one-by-one site. Length of *c*-axis drastically increased up to 10 % compared to the initial β - Ti_3O_5 structure synchronized with the displace of Ti(3) and O(5). At 6.6 GPa (10000 steps,) whole cells completed phase transition to λ - Ti_3O_5 structure. In the case of isothermal-isovolumic (NVT) calculation under uniaxial strain on *c*-axis of initial β - Ti_3O_5 structure, phase transition from β - Ti_3O_5 to λ - Ti_3O_5 was also observed at the tensile strain-induced unit cell. This phase transition was successfully observed in both classical and *ab initio* MD.

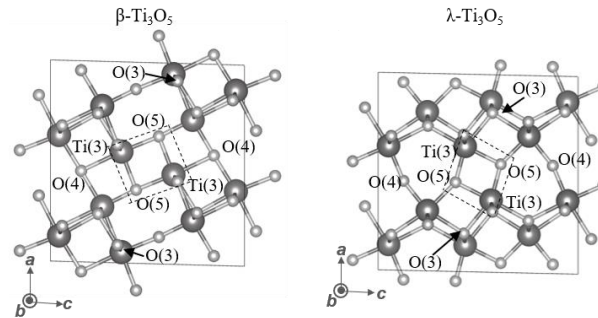


Figure 1. Crystal structure of β and λ Ti_3O_5 . Conventional unit cells with 4 chemical formulas are drawn. Thick gray spheres and thin gray spheres represent for Ti and O atoms, respectively. Inequivalent atomic sites Ti(3), O(3), O(4) and O(5), especially discussed in this thesis, are shown. Structural phase transition between β and λ phase can be interpreted as the large rotational displacement of Ti(3) and O(5) (enclosed in dashed lines,) dissociation of Ti(3) and O(4), and association of Ti(3) and O(3).

Phonon softening under uniaxial strain

Phonon softening is one of the well-known theories to discuss a mechanism of displacive structural phase transition [4]. In this theory, a frequency of the specific phonon vibration mode decreases (softening,) as the precursor phenomena to the phase transition, and its vibrational direction corresponds to the one of displacements in the phase transition. Displacement of Ti(3) and O(5) atoms occurs in the structural phase transition between β and λ -Ti₃O₅, and it is assumed to be a relationship with phonon softening. To discuss the mechanism of tensile-induced phase transition, dependence of phonon under *c*-axis uniaxial strain was calculated. The calculation was performed with OpenMX and ALAMODE code, by frozen phonon method. β -Ti₃O₅ structure with a supercell of 64 atoms (8 chemical formulas.) All of simulation cells were set as periodic boundary. As increasing lattice strain on *c*-axis, specific optical modes' frequency decreased, especially around Γ point. Also, in the case that tensile strain is applied against *c*-axis of β -Ti₃O₅, the atomic displacement direction in the vibrational modes at the minimum and the second from the minimum frequency corresponded as the one observed in the displacement phase transition. This suggests the relationship between phonon softening and strain-induced phase transition from the viewpoint of movement of atoms.

Conclusion

This research suggests the phase transition route from β -Ti₃O₅ to λ -Ti₃O₅, by tensile stress or strain, and analyzed its dynamics of an atomic displacement. Also, the mechanism of the phase transition was discussed by the relationship of phonon-softening and tensile deformation on a unit cell. It is the first time to discover the tensile-induced phase transition by MD calculation for Ti₃O₅, and to succeed in obtaining atomic-scale dynamics in a phase transition between β and λ -Ti₃O₅. Observed dynamics of atomic displacement in the phase transition was corresponded to the one that has been assumed in the previous research, yet it has not been revealed. This newly found phase transition route suggests the realization of large size single crystalline λ -Ti₃O₅, still not realized as a non-dope system, by applying tensile force against a β -Ti₃O₅ single crystal.

References

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