Development of synthesis method for λ-Ti_3O_5 using titanium chloride as a starting material and evaluation of its heat-storage properties

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Keywords: *Titanium oxide; Heat-storage material; Pressure-induced phase transition*

[Introduction] The lambda-phase trititanium pentoxide (λ-Ti_3O_5) was reported as a pressure-responsive heat-storage material that enable to preserve thermal energy in the long-term.[1], [2] In this study, we developed a synthesis method to obtain λ-Ti_3O_5 simply by using titanium chloride as a starting material.

[Experiment] A mixed solution of H_2O, $TiCl_4$, and NH_3 was prepared in a round bottle flask. The solution was stirred at 50 ℃ for 20 hours in an oil bath. The precipitation was extracted from the solution by centrifugation, washed with ethanol, and heated at 60 ℃ for 24 hours to obtain a precursor. Then the precursor was sintered at 1100 ℃ for 20 hours under a hydrogen flow rate of 0.5 dm^3 min^{-1}, obtained a black powder sample.

[Results] XRF measurement indicated that the composition formula was $Ti_{3.00(3)}O_{5.00(3)}$ (Calculated: Ti 64.22, O 35.78 wt%; Found: Ti 64.53, O 35.47 wt%). Powder X-ray diffraction (PXRD) pattern and Rietveld analysis indicated that the obtained black powder was a single phase of λ-Ti_3O_5 (monoclinic, $C2/m$; a = 9.8332(2), b =3,78568(7), c = 9.9688(2), β = 91.259(2) °) and the crystalline size was estimated 57 ± 3 nm. Pressure threshold (P_{th}) for converting 50 % of λ-Ti_3O_5 to β-Ti_3O_5 was approximately 300 MPa. The transition enthalpy (ΔH_{trans}) of the temperature-induced phase transition from pressure-produced β-Ti_3O_5 to λ-Ti_3O_5 was 7.78 ± 0.26 kJ mol^{-1} at 462 K. Next, we investigate the influence of the crystalline size on the P_{th} and the ΔH_{trans}. The examination of the relationship between crystalline size and the P_{th} and the ΔH_{trans} demonstrated that a reduction in crystalline size and an increase in the proportion of surface atoms intensify the influence of surface energy on the Gibbs free energy. This decreases the ΔH_{trans} and consequently increases the P_{th}. Understanding the relationship between the crystalline size and heat storage properties is essential for developing effective heat storage materials.

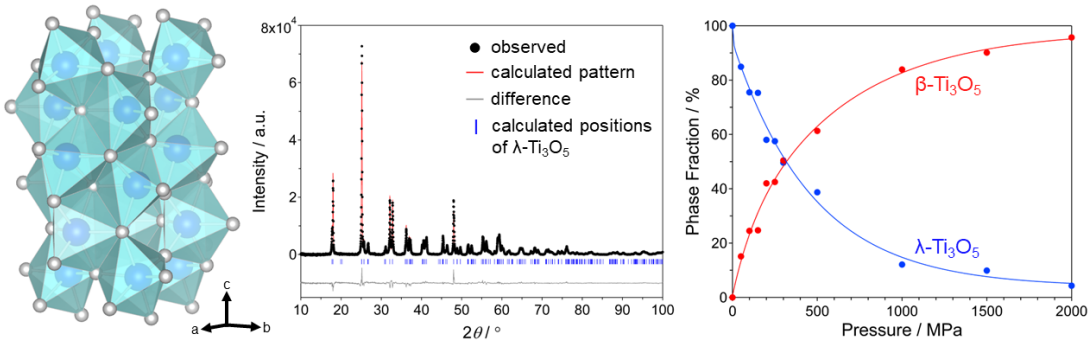

Fig. 1: Crystal structure of λ-Ti_3O_5 (left), PXRD pattern with Rietveld analysis of the obtained black powder sample (middle), and the phase fraction of λ-Ti_3O_5 and β-Ti_3O_5 (right).

1) S. Ohkoshi, et al. *Nature Chem.*, 2010, **2**, 539. 2) H. Tokoro, et al., *Nature Commun.*, 2015, **6**, 7037.