

## Powder Neutron Diffraction of Ta- and Al-doped Zn<sub>2</sub>TiO<sub>4</sub>

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When the tantalum ions are partly substituted in stead of titanium ions in Zn<sub>2</sub>TiO<sub>4</sub> accompanied by the deficiency of zinc, Zn<sub>2-x/2</sub>Ti<sub>1-x</sub>Ta<sub>x</sub>O<sub>4</sub>, oxide ion conduction appears at elevated temperatures [1,2]. From the powder density measurements and TOF neutron diffraction, this type of substitution was found to form the cation vacancies at the octahedral site of the inverse-spinel structure, contributing to the oxide ion conduction [3].

Recently, it was found that in addition to tantalum, aluminum substitution which reduces the cation deficiency also forms the solid solution, and any obvious enhancement of oxide ion conduction was not observed when equimolar tantalum and aluminum ions are substituted [4]. However, structural investigation of both Ta- and Al-doped Zn<sub>2</sub>TiO<sub>4</sub> was not made and even the position of aluminum was uncertain. In the present study, neutron diffraction experiments were carried out on  $x = 0.15$  of Zn<sub>2-x/2</sub>Ti<sub>1-x</sub>Ta<sub>x</sub>O<sub>4</sub> (ZTT) and Zn<sub>2</sub>Ti<sub>1-2x</sub>Ta<sub>x</sub>Al<sub>x</sub>O<sub>4</sub> (ZTTA) up to 500 K to clarify the conduction mechanism.

Samples of ZTT and ZTTA were prepared by conventional solid-state reaction method started from ZnO, TiO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub> and Al<sub>2</sub>O<sub>3</sub>. The calcining and sintering temperatures were selected as 1000 and 1200 °C, respectively. About each 10 g of the crushed samples were charged in vanadium cells, which were mounted in the high-temperature CTI. Neutron diffraction experiments were carried out 300, 400 and 500 K on the multi-counter type diffractometer HERMES installed in the JRR-3M reactor of JAEA [5]. The wavelength of the neutron beam was 1.8265 Å. Structure refinement was performed using Rietveld refinement program RIETAN-2000 [6].

The refined structure of ZTT at room temperature essentially agrees with that of previous one obtained by TOF neutron diffraction; the tantalum substitution and vacancy formation were made at octahedral site of the inverse-spinel type structure. On heating, any apparent structural change, e.g. symmetry or occupancy of each site, was not detected. The diffraction data of ZTTA can be also refined with relatively worse Rwp values, although additional diffraction peaks caused by ZnO were detected. Multi-phase analysis suggested the amount of ZnO was estimated as about 5 % in weight. While the tetrahedral site was occupied only by zinc ions, octahedral one was by zinc, tantalum and aluminum ions. When the Rietveld fitting was carried out assuming all the cations were stuffed and allowing the occupation factor of oxide ion to vary, the deduced occupancy of oxide ion was  $g(O) = 1.015(12)$ . This indicated that, although small amount of vacancy might be introduced in the cation site, any significant deficiency was not supposed to be occurred.

The lattice parameters, interatomic distances between cation-oxide ions, and isotropic temperature factors of oxide ions were plotted versus temperature in Fig. 1, all of which essentially grew larger with temperature. While the tetrahedral cation-oxide ion lengths show similar values (Fig. 1(b)), octahedral ones represent some discrepancy (Fig. 1(c)). This is consistent with the result of the cation distribution that tetrahedral site was occupied by Zn without deficiency in both systems whereas the octahedral position contains different species between these two systems. While isotropic temperature factors become larger with temperature in both systems, ZTTA shows apparent enhancement at 500 K comparing with ZTTA. This

also consistent with the fact that cation deficient ZTT shows oxide ion conduction at elevated temperatures while stuffed ZTTA was not. High temperature experiment was expected to show more apparent behavior. In addition, further precise investigation would reveal the oxide ion motion and oxide ion conduction mechanism of ZTT.

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1. T. Esaka, T. Ikebe and M. Kamata, *Denki Kagaku* 61 (1993)749.
2. T. Esaka, T. Ikebe and M. Kamata, *Solid State Ionics* 76 (1995)237.
3. S. Takai, T. Shinohara, A. Hoshikawa, S. Harjo, K. Oikawa, T. Ishigaki, T. Kamiyama, T. Esaka, (in preparation).
4. H. Okada, S. Takai, T. Esaka, (unpublished).
5. K. Ohoyama, T. Kanouchi, K. Nemoto, M. Ohashi, T. Kajitani and Y. Yamaguchi: *Jpn. J. Appl. Phys.* 37 (1998) 3319.
6. F. Izumi and T. Ikeda, *Mater. Sci. Forum*, 321-324 (2000) 198.

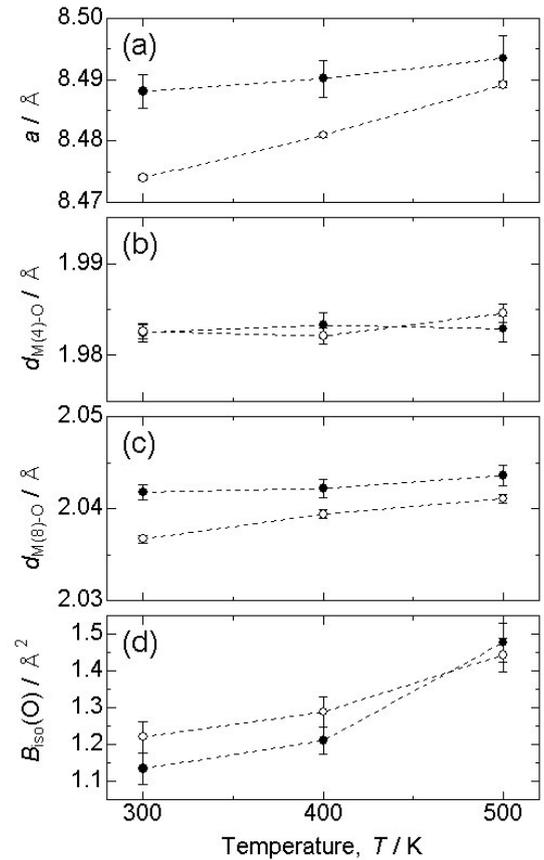


Fig. 1. Temperature dependence of (a) lattice parameters, (b) tetrahedral cation-oxide ions and (c) octahedral cation-oxide ion interatomic distances and (d) isotropic temperature factors of oxide ions.  $\bullet$  : ZTT and  $\circ$  : ZTTA.