In-situ observation of the tetragonal-cubic phase transition in the CeZrO4 solid solution

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Yashima et al. [1,2] investigated the temperature and compositional dependence of the axial ratio in the CeZrO4 solid solution by ex-situ x-ray, synchrotron x-ray and neutron diffraction measurements of quenched samples at room temperature. They reported the existence of three metastable tetragonal forms of t, t′ and t″. The three tetragonal forms belong to the P42/nmc space group. However, as no high-temperature in-situ studies of the crystal structure or cubic?tetragonal phase transition have been conducted for the CeZrO4 solid solution, the temperature dependence of the oxygen displacement and atomic displacement parameters remains an unresolved issue. In this study, we investigated the temperature dependence of the crystal structure of the CeZrO4 solid solution through in-situ neutron diffraction measurements at high temperatures.

A CeZrO4 solid solution was prepared by co-precipitation method. The Ce(NO3)3 and ZrO(NO3)2 aqueous solutions were prepared, which contained 20 mass% CeO2 and 25 mass% ZrO2, respectively. Each solution was mixed with ion-exchanged water so that 1 mass% of CeZrO4 is contained. The mixed solution was put into a 5 mass% ammonia aqueous solution. Hydroxides precipitated at this stage. After sucking filtration and washing of the resultant precipitates, the precipitate was calcined at 800 oC for 3 h. The CeZrO4 powders thus obtained were pressed into pellets, and they were sintered at 1700 oC for 5 h, and then they were annealed at 800 oC for 24 h. The cylindrical product of 19mm in diameter and of 76 mm in height was obtained after the sintering. Neutron diffraction measurements were performed in air with a 150-detector system, HERMES, installed at the JRR-3M reactor in Japan Atomic Energy Agency, Tokai, Japan. Neutrons with wavelength 1.8143 were obtained by the (311) reflection of a Ge monochromator. Diffraction data were collected in the 2? range from 5? to 150? in the step interval of 0.1?, from 296 K to 1829 K. A furnace with MoSi2 heaters [3] was placed on the sample table, and used for neutron diffraction measurements at high temperatures. Sample temperatures were kept constant within ?1?C during each data collection. The diffraction data were analyzed by the Rietveld method with a computer program RIETAN-2000 [4].

Rietveld analysis of the CeZrO4 solid solution was carried out by the tetragonal structure with the P42/nmc space group at 296-1543 K. Data at 1829 K were analyzed assuming the cubic fluorite-type structure with space group. The calculated profile is in good agreement with the observed data (Fig. 1).

The unit-cell parameters a t ’and ct ’of the CeZrO4 solid solution increased with temperature, coinciding between 1523 K and 1829 K due to the t ’-c transformation.

The axial ratio of the metastable t ’-CeZrO4 decreased from 1293 K to 1523 K. The axial ratio became unity between 1523 K and 1829 K, corresponding to the t ’-c phase transition. The oxygen displacement d(O) from the regular 8c position of the cubic fluorite-type structure can be estimated by the equation d(O) = c[0.25 ? z(O)]. The d(O) value of CeZrO4 decreased to 0.0 between 1523 K and 1829 K, corresponding to the t ’-c phase transition (Fig. 2).

The isotropic atomic displacement parameters of Ce and Zr atoms B(Ce,Zr) and oxygen atoms B(O) increased with temperature (Fig. 3). B(O) was larger than B(Ce,Zr), suggesting the higher diffusivity of oxygen ions (Fig. 3).

In the present study we have confirmed that the CeZrO4 solid solution transforms from the tetragonal t ' form to the cubic phase between 1543 K and 1829 K. The c-to-t ' phase transition of CeZrO4 is accompanied by oxygen displacement along the c axis and the increase of the c/aF axial ratio from unity.

References

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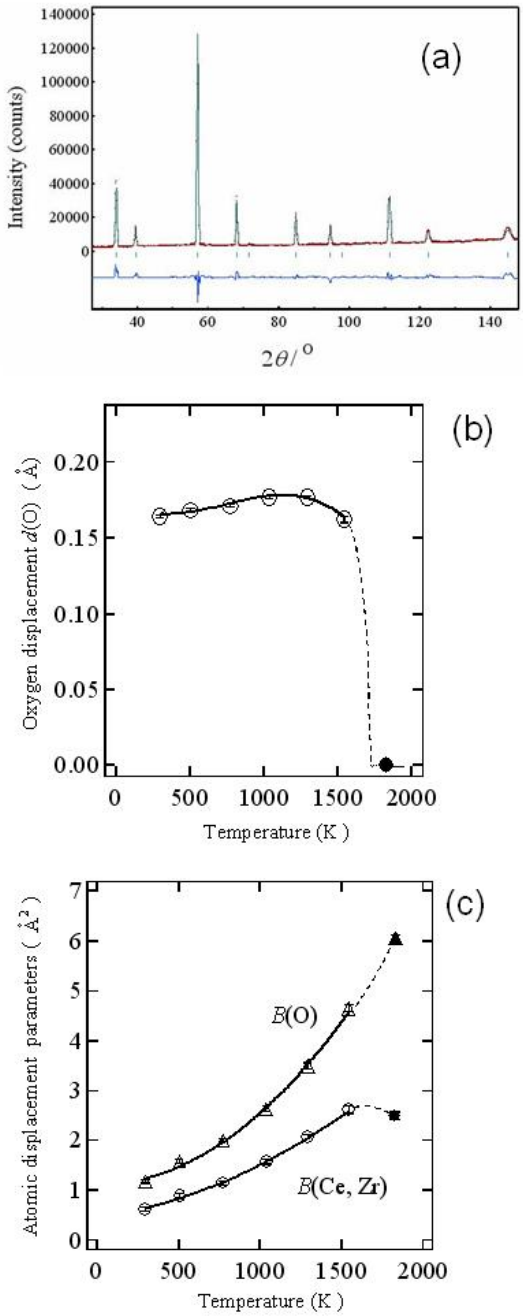

Fig. 1. Rietveld pattern (1829 K) (a), temperature dependence of oxygen displacement (b) and thermal parameters (c) of CeZrO4.