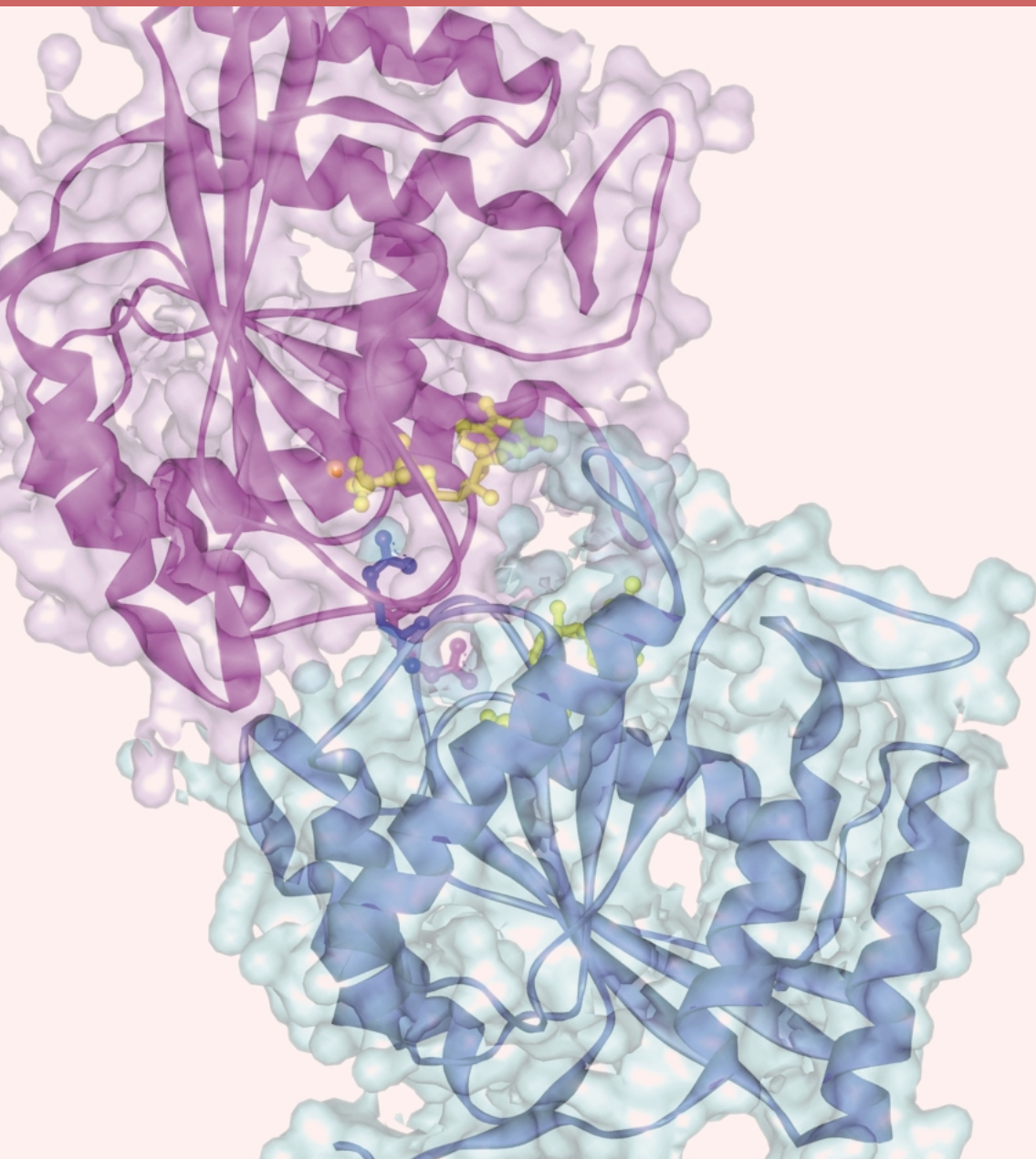


# *Highlights*



## 6-1 In-situ X-ray Diffraction Study on the Transformation Kinetics of Mantle Minerals at High Pressure and High Temperature

As the oceanic plate descends into the Earth's lower mantle below the 660 km seismic discontinuity, garnet and silicate spinel, which are the major constituent minerals in the oceanic crust and the underlying peridotite layer, respectively, cause the decomposition reaction forming silicate perovskite (the post-garnet transformation and the post-spinel transformation, Fig. 1). It has been suggested that these transformations are kinetically inhibited due to low temperatures in the plate and metastable low-pressure phases exist beyond the equilibrium boundary. Because the density increase  $\sim 10\%$  caused by these transformations is much larger than the thermal density difference between the plate and the surrounding mantle, kinetics possibly affects the style of the mantle convection by determining whether cold plates ( $\sim 700\text{--}1200^\circ\text{C}$ ) sink into the hot mantle ( $\sim 1600^\circ\text{C}$ ). Therefore, in order to understand the dynamics of the descending cold plates into the lower mantle, it is indispensable to examine the kinetics of the post-garnet and the post-spinel transformations.

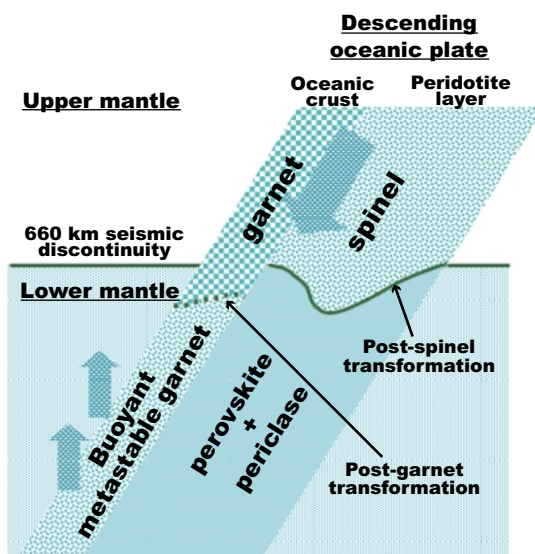


Figure 1 Schematic figure showing the cold descending oceanic plates into the hot lower mantle. The post-spinel and the post-garnet transformations near the 660 km seismic discontinuity greatly affect dynamics of the descending plates and the style of the mantle convection.

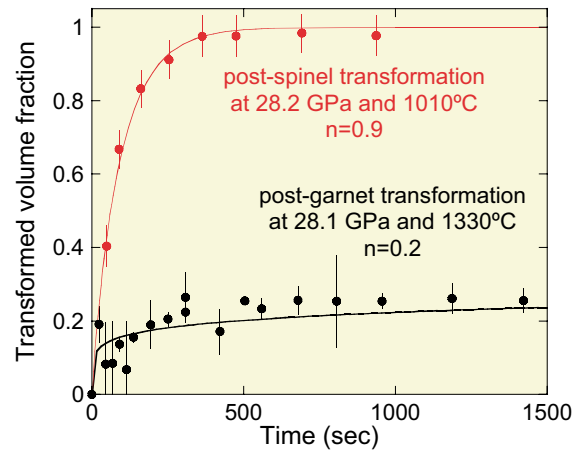


Figure 2 Transformed volume fraction with time in the post-spinel and post-garnet transformations. Curves obtained by the least-square fits of the rate equation to the kinetic data are also shown.

The kinetics of these transformations were observed at 26.7–31.0 GPa and 860–1850°C [1, 2]. X-ray diffraction patterns of the sample were taken every 10–300 seconds by the energy dispersive method using SSD. We used a high-pressure *in-situ* X-ray diffraction system with a cubic-type high-pressure apparatus (MAX-90 and MAX-III) [3]. MAX-90 and MAX-III are 400-ton and 700-ton uniaxial presses, respectively, with cubic type guide-blocks. The latter has been newly installed (2000) in BL-14C2. Pressure was generated by the double-stage system consisting of six outer anvils loading an assembly of eight truncated cubic anvils. In order to generate more than 30 GPa, sintered diamond anvils were used as the second stage anvils [4]. Figure 2 shows time dependence of the transformed volume fraction that was estimated from the decrease in the integrated intensity of diffraction lines in the parental phase. The post-garnet transformation was much slower than the post-spinel transformation.

Electron microscopy of the partially transformed sample revealed that these transformations are the grain-boundary reaction. Because the reaction rim of the decomposed assemblages was formed along the grain boundaries at the initial stage of the transformation, the overall transformation rate is controlled mainly by the growth kinetics. Based on the observed transformation mechanisms, the present kinetic data was analyzed using the rate equation  $V = 1 - \exp\{-2SX(t)\}$ , where  $V$  is the transformed volume fraction,  $S$  is the area of the grain boundary, and  $X(t)$  is the growth distance at time  $t$  [5]. The area of grain boundary can be expressed by  $3.35/d$ , where  $d$  is the grain size of the parental phase.  $X(t)$  is described by  $Kt^n$ , where  $K$  and  $n$  are constants.

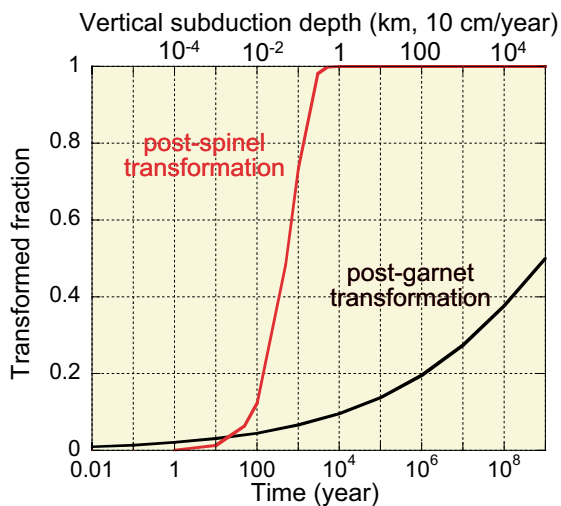


Figure 3 Rates of the post-spinel and post-garnet transformations in the descending plate into the lower mantle estimated by extrapolating the obtained kinetic data.

The  $n$ -value was very small and less than 1 in the post-garnet transformation, which means that the growth rate is time dependent and significantly decreases with time. This is different from the post-spinel transformation, in which the  $n$ -value was nearly 1 and the growth rate was almost constant. These differences in growth kinetics are believed to originate from differences in growth textures between these transformations [1, 2].

These are the first results of the direct measurement of the post-spinel and the post-garnet transformation kinetics by an *in situ* X-ray diffraction method. The rates of these decompositional transformations in the cold descending plate into the lower mantle were estimated by extrapolating the present kinetic data (Fig. 3). Our experimental results suggest that the post-spinel transformation can complete, however the post-garnet transformation is too slow to complete in geological time scales in the plates. Because a large amount of metastable garnet can survive in the descending oceanic crust into the lower mantle (Fig. 1), the oceanic crust would be buoyant in wider depth ranges at the top of the lower mantle taking the transformation kinetics into account.

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## 6-2 High-Resolution Synchrotron Radiation Powder Diffraction Study of Phase Change in Ceramic Materials

It is of vital importance to study the phase change of ceramic materials for various fields of science and engineering including physics, chemistry and geoscience. Properties of ceramic materials are strongly dependent on the existing phases and crystal structure. They often exhibit anomalies near the phase boundary. Therefore, a number of researchers have studied the phase change in ceramic materials by investigating the compositional and temperature dependence of lattice parameters through the X-ray powder diffraction technique. However, we often encounter difficulties in determination of lattice parameters near the phase boundary, because the splitting of some reflection peaks is too small to be differentiated from each other by the laboratory-based conventional X-ray diffractometer. On the contrary, the high-resolution synchrotron radiation powder diffraction method is very powerful in differentiating the reflection peaks (Fig. 4 [1]). We have performed synchrotron radiation powder diffraction experiments at BL-3A in order to investigate the phase changes in ceramic materials [1-5].

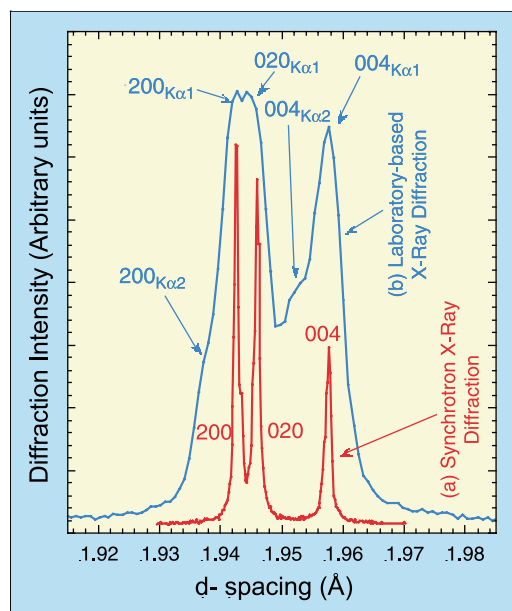


Figure 4 Comparison between synchrotron radiation and conventional X-ray diffraction profile of 004, 020 and 200 reflection peaks of  $\text{La}_{0.68}(\text{Ti}_{0.95}\text{Al}_{0.05})\text{O}_3$  obtained at 200°C. The synchrotron radiation diffraction reflection peak has a much narrower width, symmetric shape and no splitting into  $K_{\alpha 1}$  and  $K_{\alpha 2}$  components.

### Tetragonal Form with an Axial Ratio $c/a$ of Unity

Zirconia ( $\text{ZrO}_2$ ) and hafnia ( $\text{HfO}_2$ ) solid solutions as  $\text{Zr}_{1-x}\text{Y}_x\text{O}_{2-x/2}$ ,  $\text{Zr}_{1-x}\text{Ce}_x\text{O}_2$  and  $\text{Hf}_{1-x}\text{Y}_x\text{O}_{2-x/2}$  have distorted fluorite-type structure. These materials are quite important for solid oxide fuel cells and catalysis. We have investigated the compositional ( $x$ -) dependence of lattice parameters by synchrotron radiation powder diffraction experiments, in order to study the tetragonal-cubic phase change in zirconia-ceria solid solutions  $\text{Zr}_{1-x}\text{Ce}_x\text{O}_2$  [2]. Neutron and synchrotron radiation diffraction measurements have indicated a tetragonal zirconia phase with both an axial ratio of unity and internal shear deformation. The oxygen displacements from an ideal fluorite position of 0.088 and 0.078 Å are observed for the 65 and 70 mol%  $\text{CeO}_2$ - $\text{ZrO}_2$  samples, respectively. However both  $c/a$  values are  $1.000 \pm 0.001$  in these samples (Fig. 5). The  $c/a$  ratio decreases with increasing of  $\text{CeO}_2$  content and discontinuously to unity around 60 mol%  $\text{CeO}_2$  composition, while the oxygen displacement decreases continuously up to about 90 mol%  $\text{CeO}_2$ . Similar results are obtained also in  $\text{Hf}_{1-x}\text{Ce}_x\text{O}_2$  [3] and  $\text{Hf}_{1-x}\text{Y}_x\text{O}_{2-x/2}$  [4].

### In-Situ Observation of a Continuous Phase Transition in Double Perovskite [1, 5, 6]

$\text{La}_{2/3}\text{TiO}_3$ -based compounds with a double perovskite-type structure (Fig. 6(b)) are some of the most important materials in current science and engineering such as wireless technology due to their excellent electrical properties. The activation energy for oxygen ion conductivity decreases with increasing temperature. In order to study the relationship between the crystal structure and ion conductivity, we have performed high-

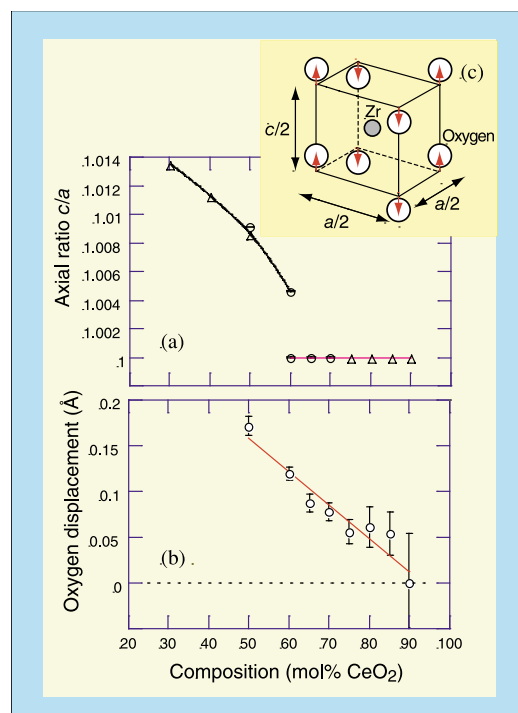


Figure 5 Compositional dependence of (a) axial ratio  $c/a$  and (b) oxygen displacement in  $\text{ZrO}_2$ - $\text{CeO}_2$  solid solutions. (c) Oxygen polyhedron around a Zr ion in  $\text{ZrO}_2$ - $\text{CeO}_2$  solid solutions.

temperature synchrotron radiation powder diffraction experiments using a furnace originally developed by Tanaka [7]. The lattice parameters  $a$ ,  $b$  and  $c$  increase with an increase of temperature (Fig. 6(a)). The  $b/a$  ratio decreases continuously with an increase of temperature and becomes unity at around 370°C. Lattice parameters

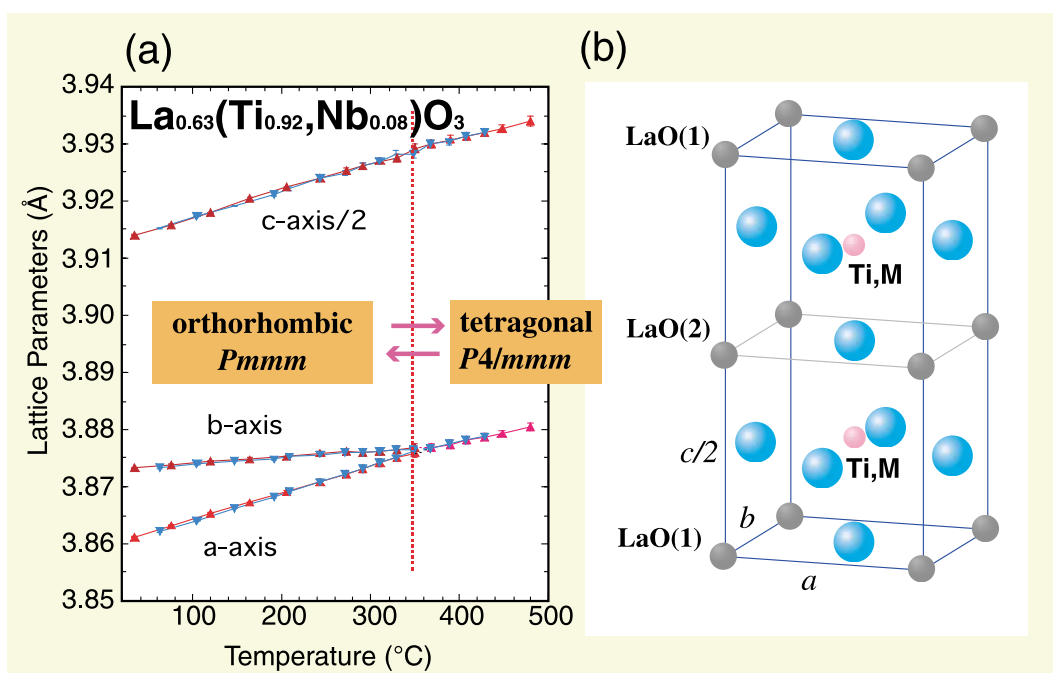


Figure 6 (a) Temperature dependence of lattice parameters of the  $\text{La}_{0.64}(\text{Ti}_{0.92}, \text{Nb}_{0.08})\text{O}_3$  compound. (b) Crystal structure of  $\text{La}_{0.64}(\text{Ti}_{0.92}, \text{Nb}_{0.08})\text{O}_3$ .

determined from the data measured on heating exhibit fairly good agreements with those measured on cooling. Taking account into the results, (I) the good agreement between the lattice parameters obtained from the heating and cooling data, (II) the continuous change in lattice parameters with temperature, the orthorhombic-tetragonal phase transition is strongly suggested to be continuous and reversible. These features of the phase transition are very new and possible explanations for the decrease in the activation energy are the phase transition and the decrease in  $b/a$  ratio with increasing temperature.

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