

## Formation of the perovskite solid solution in the system of $\text{CaTiO}_3\text{-KNbO}_3$ at high pressure and high temperature

Takaya NAGAI\*, Natsuki ISHIGURO, Yusuke HINO  
Hokkaido Univ., Sapporo, Hokkaido 060-0810, Japan

### Introduction

Silicate perovskites ( $\text{MgSiO}_3$  and  $\text{CaSiO}_3$ ) are believed to be major constituent minerals in the Earth's lower mantle. It has been known that silicate perovskites form solid-solutions by various divalent and trivalent cations substitutions. However, the solubilities of monovalent cations such as  $\text{Na}^+$  and  $\text{K}^+$  are unclear.

In this project, we worked on the  $\text{CaTiO}_3\text{-KNbO}_3$  system in order to understand the relationship between crystal chemistry and the solubility of  $\text{K}^+$  as a monovalent cation.  $\text{CaTiO}_3$  is the mineral perovskite. Since  $\text{CaTiO}_3$  perovskite is stable at ambient conditions, it should be a good analogue mineral of silicate perovskites which are stable at very high pressure. Since  $\text{KNbO}_3$  also has an orthorhombic perovskite structure at ambient conditions [1], we may expect the formation of perovskite solid solution formation of this system.

We preliminary performed high temperature synthesis at 1273 K in the  $\text{CaTiO}_3\text{-KNbO}_3$  system at an ambient pressure and found that there is no solid solution formation in the system. However, we know that the solubility of cations often changes greatly under high pressure and high temperature conditions. Thus, we studied the phase equilibrium in the system at high pressure and high temperature.

### Experimental

#### *Preparation of starting materials*

We firstly prepared gels containing Ca, K and Ti by a sol-gel method. Then we well-mixed them with a reagent grade of  $\text{Nb}_2\text{O}_5$  powders and finally made starting materials with desired chemical compositions (mol ratios:  $\text{CaTiO}_3 : \text{KNbO}_3 = 3 : 1, 1 : 1, 3 : 2$  and  $1 : 3$ ).

#### *High pressure synthesis*

Experiments of high pressure synthesis were performed by using the multi-anvil high pressure apparatus, MAX80, installed in the beam line AR-NE5C hutch. We used a multi-anvil 6-6 assembly developed by Ehime Univ. GRC

group. Heating samples were conducted by carbon tube heater and temperature was measured by W/Re (3-25 %) thermocouple. Typical heating time was for 1 hour.

#### *X-ray diffraction measurements*

X-ray diffraction patterns were measured by an energy dispersive method using a Ge-SSD fixed at 2 theta of 6 degree. Pressure was estimated by the unit cell volume of NaCl internal pressure marker. After high pressure and high temperature synthesis, temperature was quenched and pressure was released slowly to ambient pressure.

### Results and Discussion

X-ray diffraction patterns of all run products synthesized at 3 GPa and 1273 K show the coexistence of two phase orthorhombic perovskites. Judging from their unit cell parameters, it seems that the two perovskite correspond to almost pure perovskite phases of  $\text{CaTiO}_3$  and  $\text{KNbO}_3$ .

X-ray diffraction patterns of all run productus synthesized at 6 GPa and 1273 K also show the coexistence of two phase orthorhombic perovskites. However, their unit cell parameters slightly change from those of pure end members. It suggests that the small amount of  $\text{KNbO}_3$  composition incorporates into  $\text{CaTiO}_3$  perovskite and vice versa.

X-ray diffraction patterns of all run products synthesized at 8 GPa and 1273 K can be explained as a single phase of orthorhombic perovskite. Their unit cell parameters can be plotted on an interpolation between those of  $\text{CaTiO}_3$  and  $\text{KNbO}_3$ , and suggest the chemical compositions of the run products are almost same as their starting materials.

### References

[1] J.C. Chervin et al., Solid State Comm. 110, 247 (1999).

\* nagai@mail.sci.hokudai.ac.jp