

Oxygen diffusion in perovskite with different Ca/Ti ratio

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<Introduction> Calcium-aluminum-rich inclusions (CAIs) in chondrites are believed to be the first solid formed in solar nebula and are composed of refractory minerals, such as spinel, melilite, anorthite, and perovskite (CaTiO₃). Previous studies have been reported heterogeneous oxygen (O)-isotopic compositions among the CAI minerals [Clayton et al. (1973)]. The isotopic compositions are considered to be a marker of O-isotopic composition in the solar nebula [Yurimoto et al. (1998); Itoh and Yurimoto (2003); Park et al. (2012)]. Diffusion processes are important processes to affect the O-isotopic compositions of CAI minerals. To understand the effect, oxygen diffusivity of minerals should be investigated.

Perovskite crystals showed several order of larger oxygen diffusion coefficients than other CAI minerals [Gautason and Muehlenbachs (1993); Ryerson and McKeegan (1994); Sakaguchi and Haneda (1996)]. Thus, its O-isotopic compositions can provide us an important key to understand whether O-isotopic compositions of the CAI minerals have been modified or not. However, there still were a few reports on the oxygen diffusivity of perovskite, and the previously reported values are different by about one order of magnitude [Gautason and Muehlenbachs (1993); Sakaguchi and Haneda (1996)]. In this study, we focus on Ca/Ti ratio of perovskite and determined oxygen diffusion coefficients in perovskite with different Ca/Ti ratio experimentally.

<Experimental> Polycrystalline perovskite samples were prepared by a conventional sintering technique. High-purity reagent-grade powders of CaCO₃ and TiO₂ were used as the starting materials. These powders were mixed as Ca/Ti=0.098-1.002 by ball milling with PSZ balls. The powders were pressed as a sheet and were sintered at 1350 degC for 2 h in the atmosphere. Then, perovskite samples with different Ca/Ti ratio were obtained. Because of a contamination of ZrO₂ from PSZ balls, Ca/Ti ratio of the samples may differ by 0.001-0.0015 from initial value.

The samples were polished and finished by a mechanical polishing using the several grade of diamond pastes. To remove damages by the polishing, the samples were annealed at 1200 degC for 1h in the atmosphere. The samples were annealed under ¹⁸O₂ gas at 750-1050 degC for several hours. Oxygen diffusion coefficients in the samples were determined using depth profiles of ¹⁸O concentration of the samples obtained by secondary ion mass spectrometry (Cameca ims-4f).

<Results and discussion> Two contributions to the oxygen bulk diffusion mechanism are observed in depth profiles of ¹⁸O concentration obtained from Ti-rich perovskite samples. One starts near surface (diffusion A) and the other starts from about a few 100 nm depth (diffusion B) of the sample. In Ca-rich perovskite samples, only a diffusion mechanism is observed.

We found that the oxygen bulk diffusion coefficients (D_b) in Ca-rich perovskite samples were larger than that of Ti-rich samples, in both diffusion A and B. The D_b value of 950 degC in a perovskite sample prepared by a powder with Ca/Ti=0.098 was 7×10^{-13} cm²/s (diffusion A), 1×10^{-11} cm²/s (diffusion B), whereas the value of a sample prepared by a powder with Ca/Ti=1.002 was 7×10^{-10} cm²/s.

Previous reports showed ¹⁶O-poor [Ito et al. (2004)] or ¹⁶O-rich [Park et al. (2012)] perovskite in carbonaceous chondrites. It has been suggested that the former was changed from its original isotopic composition during thermal processes, the later was escaped the secondary processes. Larger oxygen diffusion coefficients of perovskite than that of other CAI minerals suggested that perovskite record the final thermal process, which the CAI experienced. Moreover, this study may suggest shorter timescale required for change of O-isotopic composition of perovskite than previously estimated and also indicates the importance of investigation on Ca/Ti ratio of perovskite to understand its oxygen diffusivity.

Keywords: Perovskite, Oxygen diffusion