Japan Geoscience Union Meeting 2010
(May 23-28 2010 at Makuhari, Chiba, Japan)

MIS012-02 会場:ファンクションルームB 時間: 5月23日09:25-09:38

合成ジルコン中における鉛のナノスケール存在状態

Nanoscale occurrence of Pb in synthetic Pb-doped zircon

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Zircon ($ZrSiO_4$, $I4_1/amd$, Z=4), is one of the most durable mineral chemically and physically. Because of its capability to accommodate trace elements such as lanthanides and actinides, zircon was proposed as a potential host for Pu immobilization in a safe disposal of high-level nuclear waste. In addition, natural zircon contains various concentrations of U and Th and has been used in U-Pb chronology.
Because Pb occurrence is crucial to understand the mechanism of discordance in U-Pb dating, it has been investigated extensively and some important aspects were provided; evidence of tetravalent Pb in zircon determined by synchrotron-based X-ray absorption fine structure (XAFS) (Kramers et al. 2009) and direct evidence of Pb substitution for Zr site evidenced by transmission electron microscopy (TEM) (Utsunomiya et al. 2004). However, a general idea of Pb behavior at the nanoscale during incorporation into zircon is still not clearly understood. In this study, the nanoscale occurrence of Pb has been investigated in Pb-doped zircon using a high-resolution TEM (HRTEM), and high-angle annular dark-field scanning TEM (HAADF-STEM).
TEM results reveal four types of Pb occurrences. Type I: Pb-rich particles in 50 - 200 nm of diameter are embedded in zircon. Most of this type of particle associates with a small hole. These nanocrystallites were identified as Pb oxide hydrate based on the selected area electron diffraction pattern (SAED). Some of them are present in grain boundary. Type II: Pb-rich phase is concentrated embedded within cleavage plane or grain boundary without euhedral shape. Type III: amorphous Pb particles are present as spherical shape in zircon structure. Type IV: Pb is diluted into the matrix zircon locating at the lattice or interstitial sites. The type IV appears to be similar occurrence to natural zircon because of the low level of bulk Pb concentration.
A presence of P in the system greatly affects the Pb occurrence in zircon. In the P-free system, Pb occurs as particles which are classified as type I without detectable Pb in the matrix zircon. In the P-rich conditions (~1.3 wt. % in bulk (Watson et al.,1997)), Pb is present not only as type I but also as various forms from type II to type IV. Appearance of type IV only in P added condition implies that the charge balance mechanism expressed by $[2P^{5+} + Pb^{2+}] = [2Si^{4+} + Zr^{4+}]$ operates during Pb incorporation into zircon.
Our results indicate that process of Pb incorporation in Pb-doped zircon is controlled by multiple experimental parameters; temperature, P and H_2O content. However, the generation of type I particles does not depend on the temperature conditions and existence of hydrothermal condition.

キーワード:ジルコン,鉛,透過型電子顕微鏡,ナノスケール

Keywords: zircon, lead, TEM, nanoscale