Chemical and optical evaluation of zircon synthesized by Li-Mo flux method

*Masahiro KAYAMA[1], Das Kaushik[2], Yuta Tsuchiya[3]

1. Department of General Systems Studies, Graduate School of Arts and Sciences, The University of Tokyo, 2. Department of Earth and Planetary Systems Science, Hiroshima University, 3. Department of Biosphere-Geosphere Science, Okayama University of Science

Zircon, $ZrSiO_4$ phase occurring in various types of terrestrial and extraterrestrial rocks, is an important mineral to interpret the geological history. Crystallization, metamorphic, and sedimentary ages of zircon in the rocks can be determined by the radioactive elements. The zoning textures and Ti content in zircon reflect the thermal history of the magmatic and metamorphic processes. Furthermore, the elementary and structural features of zircon easily change during hydrothermal alteration. Natural zircon shows a decrease of the crystallinity, finally leading to amorphization, as a process of metamictization by radiations from radioactive elements in geological time. Zircon in impactite and meteorites often records an impact event of the host body as the shock-induced microstructure and texture. Such useful information on igneous, metamorphic and sedimentary processes have been obtained from microanalyses (e.g., electron microscope, SHRIMP, LA-ICP-MS, and Raman spectroscopy) of zircon. Synthetic zircon has been available as a standard material for accurate microanalyses, e.g., highly-pure synthetic zircon for checking sample background and a starting material for high-pressure and -temperature experiments to reproduce the metamorphic process and hydrothermal alteration in the geological events. Therefore, in this study, zircon was synthesized by the Li-Mo flux method reported by (Hanchar et al. 2001) using a heating furnace under various conditions.

Synthetic ZrO_2 and SiO_2 powder samples and Li_2SiO_3, Li_2MoO_4 and, MoO_3 flux were put into an unwelded platinum crucible (100 cc) in the heating furnace at room temperature (RT) and ambient pressure. Temperature in the heating furnace rose initially from RT to 1250 °C for 18 h, then kept at 1250 °C for 10 h, decrease from 1250 to 1000 °C for 500, 125, 63, 32, and 12 h (cooling rate of 0.5, 2.0, 4.0, 7.8, and 20.8 °C/h, respectively), and finally dropped from 1000 °C to RT for 25 h. All the recovered samples were measured by the optical and scanning electron microscopes, cathodoluminescence (CL) microscopy, and Raman spectroscopy. WDS analysis by EPMA and LA-ICP-MS measurements were performed for only zircon synthesized at a cooling rate of 0.5 °C/h.

All of the zircon grains synthesized at each cooling rate show a large amount of euhedral single crystals with inherent crystal planes and a few to several hundreds of micrometer size under an optical microscope. The crystal grain size seems to decrease with the cooling rate from 4.0 to 20.8 °C/h and show almost no change below 4.0 °C/h, implying that all of the dissolved SiO_2 and ZrO_2 were separated completely from the flux above 4.0 °C/h to form $ZrSiO_4$ crystals. CL microscopy revealed that there are oscillatory and sector zoning textures in all of the synthetic zircon, of which the shapes are corresponding to crystal planes of the zircon (that is, outer rims) observed in an optical microscope. WDS analyses of the major chemical composition of the zircon at 0.5 °C/h show SiO_2, ZrO_2, HfO_2 contents of 33.02, 66.46, and 1.79 wt%, respectively. Chemical compositions of these elements are homogeneous within the single crystals. As a result of WDS analyses of the zircon, trace elements of Y_2O_3, Al_2O_3, ThO_2, P_2O_5, Yb_2O_3, CaO, Nb_2O_5, UO_2, and Sc_2O_3 are below 0.005 wt% in content or undetected. LA-ICP-MS analyses of the zircon indicate that Y and Nb contents reach 2.6 and 1.0 ppm, and La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Pb, Th, and U were below 1 ppm or detection limit. Raman spectroscopy of the synthetic zircon at

0.5 °C/h calibrated using a Kr bright line exhibits pronounced peaks at 974 and 1008 cm^{-1}, both of which the peak positions are corresponding to theoretical values of zircon unaffected by radiations, that is, metamictization. These facts imply that zircon crystals synthesized here are high quality and is expected to be used as a standard material for various microanalyses and experimental replication.

Keywords: Zircon, Synthesis, Li-Mo flux

