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Experimental study of ZrF_6^{2-} and HfF_6^{2-} stability in hydrothermal solutions

MARIIA TARNOPOLSKAIA, IRINA NIKOLAEVA, ANDREW BYCHKOV AND TATIANA LUBKOVA

Lomonosov Moscow State University

Presenting Author: mashatarnopolskaya@yandex.ru

We developed a new method to study the fluoride complexes of zirconium and hafnium at temperatures of 250-350°C and a saturated vapor pressure of water and 400-450°C degrees and a pressure of 1 kbar. Experimental study of the solubility of ZrO_2 and HfO_2 depending on pH values controlled by NaF-HF buffer. Since hydrofluoric acid is weak, this solution acts as a pH buffer and allows solubility experiments to be carried out at a constant fluorine content. The experiments were carried out in autoclaves with a volume of 50 cm^3 (alloy 2.4872) with a copper gasket. The phase was placed on the bottom of an autoclave, which will be filled with a solution with different ratios of HF and NaF with a total fluorine concentration of 0.1 mol/kg. The content of elements in the experimental solutions was determined by two methods. High-resolution mass spectrometry with ionization in inductively coupled plasma on an ELEMENT2 device (ICP-MS). The second method is energy dispersive X-ray fluorescence analysis (EDXRF) on the ThermoScientific NITON FXL 950 spectrometer for cases of high concentrations (hundreds and thousands of g/kg). Program OptimA was used for calculating the Gibbs free energies from the experimental data. The results showed that ZrF_6^{2-} and Hf_6^{2-} predominate in near-neutral solutions and provide the transport and deposition of zircon. The difference in the stability constants of such complexes can explain the distribution of hafnium in zircons. This work was supported by RSF project 19-17-00200.