

Single crystal structure analyses by XRD and local structural analyses by XAFS on natural Ce-perovskite and Nb-perovskite

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As a perovskite type compounds ABO_3 , minerals with various compositions are occurred from the Earth's crust to the lower mantle. There are few detailed structural studies of natural perovskite-type minerals which easily contains rare earth elements and various kinds of heavy metals. In this study, we conducted a comparative study on Ce-perovskite from Russia, Kola Peninsula and Nb-perovskite from USA, Arkansas. We report on structural properties of solid solution, local structural characteristics of contained elements and irregularities in structure due to radioactive elements. The chemical compositions were determined using a scanning electron microscope SEM JSM-7001F, JEOL and an energy dispersive X-ray spectrometry EDS INCA SYSTEM, Oxford. The local structures and oxidation states were analyzed by XAFS analysis using BL-9C and NW10A beam line at High Energy Accelerator Research Organization (KEK). The single crystal structure analyses were performed using Rigaku XtaLAB Super Nova. As a result of chemical analysis and structural analysis, both minerals were tetragonal perovskite: Ce-perovskite ($Ca_{0.816} Na_{0.077} Ce_{0.045} La_{0.018} Nd_{0.018} Pr_{0.005} Ag_{0.004} Sm_{0.003} Dy_{0.002} Tb_{0.002} Eu_{0.001} Gd_{0.001} Pm_{0.001} Ho_{0.001} Lu_{0.001} Sr_{0.001}$)_{0.996} ($Ti_{0.942} Fe^{2+}_{0.007} Fe^{3+}_{0.013} Nb_{0.017} Zn_{0.012} Ge_{0.007} W_{0.003}$)_{1.002}O₃, space group *Pbnm*, $a = 5.41620(3)$, $b = 5.48350(3)$, $c = 7.70340(5)$. Nb-perovskite ($Ca_{0.937} Ce_{0.021} Na_{0.020} La_{0.015} Sr_{0.003}$)_{0.996} ($Ti_{0.730} Nb_{0.122} Fe^{3+}_{0.108} Al_{0.020} Zr_{0.009} V_{0.008}$)_{0.997}O₃, space group *Pbnm*, $a = 5.40260(3)$, $b = 5.46750(2)$, $c = 7.67360(3)$. A slight inhomogeneity of the composition and a domain structure in the crystal were observed in the compo- images. It was revealed that the oxidation state of Fe in Ce-perovskite and Nb-perovskite is largely different state by the comparison of the XANES spectra. The total valence of each A and B site was almost divalent and tetravalent in both perovskites, The charges are balanced in sites by the substitution of Na⁺ and REE³⁺ at the A site and the substitution of Fe and Nb⁵⁺ at the B site. These solid solutions take large values of Debye-Waller factors. In particular, Ce-perovskite has a particularly large value due to the influence of contained radioactive elements. It can be interpreted that irregularization corresponding to local metamictization occurs due to radioactive decay of contained actinoid elements.

Keywords: perovskite, structure refinement, XAFS, local structure, radioactive element