Crystal structure and local structures of natural perovskite-type (Na,REE,Ca)(Ti, Nb)O_3 loparite by single crystal diffraction and XAFS analyses

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The perovskite type compound ABX_3 expresses various physical properties such as ferroelectricity and piezoelectricity, symmetry changes according to composition, pressure and temperature, and various deformations of framework constituted by BX_6 octahedral occur. Even in a solid solution, ferroelectricity, para electricity, superionic conductivity and the like are developed. Recently, it has attracted attention as a material for solar cells.

The perovskite-type minerals, which exist in the Earth’ s mantle, are one of the major host mineral of trace elements such as Th and REE. However, there are few detailed studies on rare earth elements and various heavy metals contained in naturally occurring perovskite-type minerals. In this study, we report on structural properties of solid solution, local structural characteristics of contained elements and irregularities due to radioactive elements, etc.

Analysis of chemical composition using SEM JSM-7001F manufactured by JEOL and EDS INCA SYSTEM manufactured by Oxford, and BL-9C and NW10A of KEK were used analysis of local structures and oxidation states by XAFS analysis and refinement of single crystal structure using Rigaku XtaLAB Super Nova.

The mineral produced from, Mt. Khibiny, Kola, Russia, which we treat as samples, is the solid solution with Lueshite $Na^{+}Nb^{5+}O_3$, Loparite $Na^{+}REE^{3+}Ti^{4+}{}_2O_6$, Perovskite $Ca^{2+}Ti^{4+}O_3$, Tausonite $Sr^{2+}Ti^{4+}O_3$ as end members. (Mitchell and Chakhmouradian 2000) SEM-EDS analysis reveal that there are albites mainly composed of $NaAlSi_3O_8$ at the rim. Therefore, we performed single crystal X-ray diffraction experiment with untwinned crystals picked up from the center.

Many discussions have been made on the crystal structure of Loparite. (Haggerty and Mariano 1983, Vlasov 1966, Mitchell 1996, Zubkova et al. 1998, Chakhmouradian et al. 1999, Mitchell et al. 2000) We attempted to analyze rhombohedral, tetragonal and tetragonal crystals which have been mentioned in previous research using this sample. Rhombohedral crystal: space group *R-3c*, a = 5.5077(2), c = 13.4906(5), Tetragonal crystal: space group *I4/mcm*, a = 5.5166(6), c = 7.7814(10), Ortho crystal Space group *Pbnm*, a = 5.5142(5), b = 5.5085(7), c = 7.7961(8) From more precise structural analysis, we will discuss the phase transition of Loparite structure etc.

From the shape of the XANES spectrum of Fe by spectral analysis, it turned out that the oxidation state of Fe contained is divalent, similar to the Ce-perovskite we investigated last time. In the Ti K-edge spectrum, it can be seen that the local distortion around Ti is considerably large from the peak intensity of pre-edge. With the substitution of Nb, the local strain of Ti at the octahedral site in the solid solution is larger than the $CaTiO_3$ end component, and the electron transition probability from 1s to 3d orbital is increasing. In the Th L3-edge spectrum, XANES is remarkable, and it can be interpreted that the actinoid element Th changes to U by causing radioactive decay, and irregularization corresponding to local metamictization

occurs.

Keywords: perovskite, XAFS, structure refinement, Loparite

