別紙様式８

研究主論文抄録

論文題目
第５・６周期元素を含有する希少鉱物の結晶構造と電子状態の精密解析

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主論文要旨

Minerals formed on Earth are generally described using chemical composition and crystal structure. Most minerals form solid solutions of two or more end-members. The crystal structure of a mineral is determined by its chemical composition, the temperature and pressure at which it crystallizes. Therefore, the crystal structure of minerals remains its past history, and the physical property changes. However, the detailed crystal structures of rare minerals that are not major phases are unknown. In this study, I attempted to understand the past records and evaluate the physical properties of rare minerals based on their unique crystal structures. In order to measure changing in lattice constant and the electronic states of the atoms with changes in chemical composition in minerals, I performed some precise analysis using single crystal X-ray diffraction and XAFS method.

In Chapter 2, structural analysis of Ce- and Nb-perovskites containing Fe, Zr, Nb, and rare earth elements (REEs) in $CaTiO_3$ perovskite was performed using single-crystal X-ray diffraction and X-ray absorption near-edge structure (XANES) analyses. In Ce- and Nb-perovskites, the total charges at the A- and B-sites achieved near-ideal divalent and tetravalent states such as $Ca^{2+}Ti^{4+}O_3$, respectively, due to complex elemental substitutions. Local distortions around Ti in the perovskite solid solutions were greater, and the pre-edge features of the Ti atoms in Ce- and Nb-perovskites were different from those in pure $CaTiO_3$. The valence states and local structures of Fe in Ce- and Nb-perovskites were significantly different. The existence of divalent Fe^{2+} at the B-site in Ce-perovskite was confirmed. It is presumed that the displacement ellipsoids of all atoms and local irregularities in Ce-perovskite increase owing to the radiative decay of the actinoid element Th. I reconfirmed that the composition and three-dimensional structure of perovskite-type structures were flexible and caused various structural

changes.

In Chapter 3, I present the structure refinement and XANES study of two gold-silver-tellurides, Au1-xAgxTe2, krennerite (x = 0.11-0.13) and sylvanite (x = 0.29-0.31), and I compare them to the prototype structure of calaverite (x = 0.08-0.10). Whereas the latter is well-known for being incommensurately modulated at ambient conditions, neither krennerite nor sylvanite present any modulation. This is attributed to the presence of relatively strong Te-Te bonds in the two minerals (bond distances < 2.9 Å), which are absent in calaverite (bond distances > 3.2 Å). In both tellurides, trivalent gold occurs in slightly distorted square planar coordination, whereas monovalent gold, partly substituted by monovalent silver, presents a 2+2+2 coordination, corresponding to distorted rhombic bipyramids. The differentiation between bonding and non-bonding contacts is obtained by computation of the Effective Coordination Number (ECoN). The Charge Distribution (CHARDI) analysis is satisfactory for sylvanite but not for krennerite, showing the former can be described as a Madelung-type compound, while the latter is not, despite the presence of Te-Te in both structures. This might be related by the higher covalency of the Te-Te bond in krennerite, pointed out by the XANES spectra.

In Chapter 4, I focused on Rh-rich and Ir-poor erlichmanite-laurite OsS2-RuS2 solid solutions have been discovered at placers in Haraigawa, Misato-machi, Kumamoto, Japan. Microprobe analysis was performed to identify solid solutions containing few sub-components other than Rh. Approximately 10 at% Rh was found to be present in the solid solutions. Structural refinement was performed using four natural samples which have different chemical compositions. The unit-cell parameters for the solid solutions containing Rh from Haraigawa varied from 5.61826(6) to 5.63142(8) Å. The (Os, Ru, Rh)–S distances in the Os1-x-yRuxRhyS2 system were almost constant with a small variation of 0.001 Å. Conversely, the S-S distances varied significantly, with variations approaching 0.1 Å. Rh substitution of Os rather than Ru showed a larger impact on the crystal structure. The bulk Debye temperatures were estimated from the Debye-Waller factor for the sulfide site. The bulk Debye temperatures of pure OsS2 and RuS2 were 688 K and 661 K, respectively, which suggests that the melting point of erlichmanite is higher than that of laurite. The high Debye temperature of OsS2 is inconsistent with the crystallisation of laurite prior to erlichmanite from the primitive magma, which suggests that f(S2), rather than temperature, is the main cause of the known crystallisation order.