

Syntheses, single crystal structure analyses of scheelite-powellite $\text{CaW}_{1-x}\text{Mo}_x\text{O}_4$ solid solutions and unique occurrence in Jisyakuyama skarn deposits

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Many synthetic experiments for scheelite-powellite solid solutions have been reported as research on fluorescent materials. In the system it is known that a complete continuous solid solution is formed even at room temperature. In this study, we have carried out the chemical analyses, single crystal structural analyses and detail description of occurrence on scheelite-powellite minerals in Jisyakuyama skarn deposits. Syntheses of single crystals of solid solution were performed in a wide compositional range. The chemical compositions were determined by JEOL scanning electron microscope and EDS, INCA system. We have carried out the crystal structure refinements of the scheelite-powellite $\text{CaW}_{1-x}\text{Mo}_x\text{O}_4$ solid solutions ($x=0.0-1.0$) by RIGAKU single-crystal structure analysis system RAPID. The final R factors were around 1-3%. The lattice constants, interatomic distances and other crystallographic parameters for the solid solution change uniquely with composition and it was confirmed as a continuous solid solution. As the result of structural refinements of natural products and many solid solutions, we confirm that most large natural single crystals have compositions at both endmembers, and solid solution crystals are rare. Although at Jisyakuyama skarn deposit, Fukuchi, Fukuoka, Japan, shows a simple occurrence formed by penetration of hot water into limestone cracks. A unique occurrence of scheelite-powellite $\text{CaW}_{1-x}\text{Mo}_x\text{O}_4$ minerals is observed in the skarn deposit. Single crystals of scheelite endmember + powellite endmember + solid solution with various compositions form an aggregate in the deposit. Crystal shapes of powellite and scheelite are pseudomorphic (platy moribdenite morphology) and allotriomorphic, respectively. Many solid solution crystals are accompanied by scheelite endmember and a small compositional gap is only observed near powellite endmember. The above unique occurrence can be explained with the change of sulfur partial pressure and oxidation conditions. Scheelite and MoS precipitate at the beginning of the mineralization process. MoS changes to powellite remaining shape as a pseudomorph by subsequent oxidation with Ca. As the oxidation progresses, the Ca (W, Mo) O₄ solid solution has a wide compositional range and is produced in the fine grain aggregate. We also try to lead to giving restrictive conditions to elucidate the mineralization process.

Keywords: Scheelite-Powellite solid solution, precise structure analysis, pseudomorph crystal