Crystal growth of pyromorphite - mimetite series Pb5(XO4)3Cl (X=P, As) from CsCl flux

Mikio Masaoka[1]; # Atsushi Kyono[2]; Tamao Hatta[3]; Mitsuyoshi Kimata[4]

[1] Collage of Natural Sci., Univ. of Tsukuba; [2] Earth Evolution Sciences, Univ. of Tsukuba; [3] JIRCAS; [4] Inst. Geosci., Univ. Tsukuba

http://www.geo.tsukuba.ac.jp/Mineralogy_Web/kyono_HP/index.html

Pb5(PxAs1-xO4)3Cl (0  x  1) single crystals were successfully grown by a flux method using cesium chloride solvent in N2 gas from stoichiometric mixture of pyromorphite and mimetite fine powder as a precursor. Individual euhedral crystals which were transparent and colorless consist of a hexagonal prism shape topped by a hexagonal pyramid, elongate [001] with a length-to-width ratio of approximately 1:5. The diameter of the crystals ranges from 0.1 to 2.0 mm and the length is in the range between 0.5 and 8.0 mm, but most crystals do not exceed 1.0 mm in length. X-ray powder diffraction, electron microprobe analysis, and infra-red examination were used to determine the chemical compositions and the solid-solution sequence of Pb5(XO4)3Cl (X = P, As) phases. These crystals were chemically fairly homogeneous and never exhibit a compositional zoning of P and As. The pyromorphite-mimetite series has complete solid solution between P and As with ideal composition Pb5[(P, As)O4]3Cl. The a and c lattice parameters increase constantly from pyromorphite to mimetite and across the solid solution vary continuously. A compositional variations in the solid solution are observed apparently in infrared absorption spectra between 1200 and 400 cm-1 where the (P,As)-O vibrational bands appear. The shape and the total intensity of the absorption bands provide a reliable indication of P and As contents in the solid solution phases. Stopping the N2 supply into the furnace, crystals lightly tinged with yellow are formed together with transparent colorless crystals from the synthesis which were performed with a starting material having a pyromorphite/mimetite ratio of 0 : 100 and 50: 50, respectively. The crystalline colorless and yellow materials display identical X-ray powder patterns and infrared absorption spectra. Furthermore, there is no significant difference in chemical compositions between a colorless and yellow crystal. In XPS measurements, although typical detection limits for most trace elements were 1000 ppm, the crystals colored yellow contain substantially no impurities to alter the electronic properties and to produce a color development. Suitable relationship for a color development process can be found in binding energies in XPS spectra. The O1s binding energies increase with being colored strongly into the crystals. The O1s binding energy for yellow tinged crystal can shift from 530.65 to 530.73 eV depending on the degree of a color development. Moreover, The O1s binding energy for green pyromorphite and yellow mimetite naturally occurred are greatly enhanced to 531.44 and 531.11 eV, respectively. This color development process in a pyromorphite-mimetite complete solid solution series between P and As would provide a geological parameter reflecting the environmental concentration of oxygen during the crystal growth.