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An X-ray Rietveld study of piemontite on the join $Ca_2Al_3Si_3O_{12}(OH)$–$Ca_2Mn^{3+}_3Si_3O_{12}(OH)$ formed by hydrothermal synthesis

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ABSTRACT

Mn^{3+} distribution at octahedral M1, M2, and M3 sites of piemontite and its effect on structural changes were investigated by X-ray Rietveld analysis of synthetic $Ca_2Al_{3-p}Mn^{3+}_pSi_3O_{12}(OH)$ piemontites. The material studied was synthesized from starting materials of $Ca_2Al_{3-q}Mn^{3+}_qSi_3O_{12.5} + H_2O$ in hydrothermal experiments with P_{fluid} of 200 and 350 MPa and temperature of 500 °C. Piemontites crystallized as single phases from $q = 0.5$, 0.75, 1.0, and 1.1 starting materials, whereas minor amounts of bixbyite and parawollastonite were associated with those synthesized from $q = 1.5$ and 1.75 starting materials. EPMA analyses of synthetic piemontites showed that the maximum Mn^{3+} content was 1.3(1) apfu. Site preference of Mn^{3+} at the octahedral sites is M3 > M1 >> M2. Mn^{3+} occupancies (g) at the M3 and M1 sites are correlated with the p-value in piemontite as $g^{M3} = -0.20p^2 + 1.00p$ and $g^{M1} = 0.23p^2 - 0.06p$, respectively, where $0.0 \le p \le 1.3$. With increasing p-value, the mean M3-O and M1-O distances of piemontites increase, but the M1-O1 distance and the O5-Si3-O6 angle change nonlinearly due to the Jahn-Teller effect. The nonlinear variations of the a and c parameters with increasing p are caused by changes in the M1-O1 distance and the O5-Si3-O6 angle, respectively. The M3 octahedra, which are more distorted than the M1 octahedra, become more tetragonally compressed with increasing Mn^{3+} at the M3 site, due to the substantial increase of the M3-O1 distance.