

Temperature dependence of Fe^{3+} , Al and Ga distributions and local domain structure in synthetic Ca-clinopyroxene

AKASAKA, Masahide^{1*}; HAMADA, Maki²; NAGASHIMA, Mariko³; EJIMA, Terumi⁴

¹Dep. Geoscience, Shimane Univ., ²School of Nature system, Kanazawa Univ., ³Dept. Earth Sci., Yamaguchi Univ., ⁴AIST

Distribution of Fe^{3+} , Al^{3+} and Ga^{3+} among octahedral and tetrahedral sites in synthetic esseneite (CaFeAlSiO_6)- and ($\text{CaFe}^{3+}\text{GaSiO}_6$)₉₀($\text{CaGa}_2\text{SiO}_6$)₁₀-clinopyroxenes at 800 and 1200 °C were investigated using ⁵⁷Fe Mössbauer and X-ray Rietveld methods to find a relation between site occupancies of trivalent cations at the octahedral and tetrahedral sites and ionic sizes of trivalent cations. The esseneite was synthesized from oxide mixture using sintering technique at 1200 °C in air. The $\text{FeGaTs}_{90}\text{GaTs}_{10}$ -Cpx was crystallized from glass starting material at 1200 °C in air. The Cpxs synthesized and those annealed at 800 °C were analyzed using ⁵⁷Fe Mössbauer spectroscopic and X-ray Rietveld methods. In the synthetic esseneite, ^{VI} Fe^{3+} :^{IV} Fe^{3+} -ratio at 800 °C was determined as 82(1):18(1) by Mössbauer method and 78.2(5):21.8(5) by Rietveld method, whereas, at 1200 °C, 79(1):21(1) by Mössbauer method and 77(1):23(1) by Rietveld analysis. The resulting Fe^{3+} populations at octahedral M1 and tetrahedral T sites in the synthetic esseneite are $\text{Fe}^{3+}0.782(5)\text{-}0.82(1)$ apfu and $0.218(5)\text{-}0.18(1)$ apfu, respectively. In the synthetic Fe^{3+} -Ga-Cpx, ^{VI} Fe^{3+} :^{IV} Fe^{3+} -ratio at 800 °C was 74(3):26(2) (Mössbauer analysis data) and 78(1):22(1) (Rietveld analysis data), while, at 1200 °C, 71(3):29(1) (Mössbauer analysis data) and 67(1):33(1) (Rietveld analysis), which results in populations at the octahedral M1 and tetrahedral T sites of $[\text{Fe}^{3+}0.67(1)\text{-}0.70(1)\text{Ga}_{0.33\text{-}0.30}]^{\text{M1}}[\text{Si}_{1.0}\text{Fe}^{3+}0.23\text{-}0.20]$

$\text{Ga}_{0.77\text{-}0.80}]^{\text{T}}$ (O = 6) at 800 °C, and $[\text{Fe}^{3+}0.64(1)\text{-}0.60(1)\text{Ga}_{0.36\text{-}0.40}]^{\text{M1}}[\text{Si}_{1.0}\text{Fe}^{3+}0.26\text{-}0.30\text{Ga}_{0.74\text{-}0.70}]^{\text{T}}$ at 1200 °C. This result indicates the temperature dependence of Fe^{3+} , Al^{3+} and Ga^{3+} distributions between M1 and T sites. However, it is evident that, even at different temperatures, distributions of Fe^{3+} , Al^{3+} and Ga^{3+} between M1 and T sites are well correlated with the ratio of ionic radius of larger Fe^{3+} -cation against smaller Al^{3+} and Ga^{3+} , as Akasaka et al. (1997) indicated. Another finding in this study is the splitting of a ⁵⁷Fe Mössbauer doublet by Fe^{3+} at M1 site into two doublets. This indicates existence of short-range domain structure by two kinds of M1 sites with slightly different distortions, which cannot be detected by X-ray diffraction.

Keywords: clinopyroxene, Mossbauer analysis, X-ray structural refinement, Crystal chemistry, ionic distributions, temperature dependence