

Distribution of cations at two tetrahedral sites in Ca2MgSi2O7-Ca2Fe3+AlSiO7 series synthetic melilite and its relation to incommensurate structure

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Distribution of Fe3+ between two different tetrahedral sites (T1 and T2) and incommensurate structure of synthetic melilites, W2T1T22O7, on the join Ca2MgSi2O7 (åkermanite: Ak)-Ca2Fe3+AlSiO7 (ferrialuminium gehlenite: FAGeh) were studied using 57Fe Mössbauer spectroscopy, X-ray diffraction at room and 200°C, and high-resolution transmission electron microscopy. Melilites were synthesized from starting materials with compositions of Ak100, Ak80FAGeh20, Ak70FAGeh30 and Ak50FAGeh50 by sintering at 1200-1350 °C and 1 atm. The average chemical compowere Ca2.015Mg1.023Si1.981O7 (Ak100), Ca2.017Mg0.788Fe3+0.187Al0.221Si1.791O7 sitions Ca1.995Mg0.695Fe3+0.258Al0.318Si1.723O7 (Ak69FAGeh25Geh6) (Ak78FAGeh19Geh3), and Ca1.982Mg0.495Fe3+0.449Al0.519Si1.535O7 (Ak49FAGeh44Geh7), respectively.

The site populations at the T1 and T2 sites determined by the Rietveld analyses were [0.788Mg+0.054Fe3++0.158Al]T1[0.056Fe3++0.153Al+1.791Si]T2 for Ak78FAGeh19Geh3, [0.695Mg+0.105Fe3++0.200Al]T1[0.112Fe3++0.165Al+1.723Si]T2 for Ak69FAGeh25Geh6 and [0.495Mg+0.173Fe3++0.332Al]T1[0.281Fe3++0.184Al+1.535Si]T2 for Ak49FAGeh44Geh7 (apfu: atoms per formula unit), respectively. The results indicate that Fe3+ distributes at both the T1 and the T2 sites. The mean T1-O distance decreases with the substitution of Fe3+ + Al3+ for Mg2+ at the T1 site, whereas the mean T2-O distance increases with substitution of Fe3+ + Al3+ for Si4+ at the T2 site, causing decrease in the a dimension and increase of the c dimension.

The existence of incommensurate structure in all synthetic melilites at room temperature was confirmed by Mössbauer and CuKa1 X-ray line profile analyses. The Mössbauer spectra of the melilites consisted of two doublets assigned to Fe3+ at the T1 site and two or three doublets to Fe3+ at the T2 site, and imply the existence of multiple T1 and T2 sites with different site distortions, respectively. The two T1 sites are not influenced by ionic substitution. Conversely, the splitting of T2 sites becomes more significant with the substitution of Fe3++Al3+ for Si4+, which results in the increase of volume and site distortion of the T2O4-tetrahedra. Thus, it is revealed that the incommensurate structure is formed by not only T1 sites with different distortions, but also T2 sites with different distortions.