

Distribution of cations at two tetrahedral sites in $\text{Ca}_2\text{MgSi}_2\text{O}_7$ - $\text{Ca}_2\text{Fe}^{3+}\text{AlSiO}_7$ series synthetic melilite and its relation

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Synthetic melilites, $\text{W}_2\text{T}_1\text{T}_2\text{O}_7$, were analyzed to determine the distribution of Fe^{3+} between two different tetrahedral sites (T1 and T2), and the relationship between ionic substitution and incommensurate structure in melilite. Melilites on the join $\text{Ca}_2\text{MgSi}_2\text{O}_7$ (kermanite: Ak)- $\text{Ca}_2\text{Fe}^{3+}\text{AlSiO}_7$ (ferrialuminium gehlenite: FAGeh) system were synthesized from starting materials with compositions of Ak_{100} (100Ak), $\text{Ak}_{80}\text{FAGeh}_{20}$ (80Ak), $\text{Ak}_{70}\text{FAGeh}_{30}$ (70Ak) and $\text{Ak}_{50}\text{FAGeh}_{50}$ (by sintering at 1200-1250 °C and 1 atm. The synthetic melilites were analyzed using X-ray powder diffraction, ⁵⁷Fe Mossbauer, and high-resolution transmission electron microscopic methods. The average chemical compositions and end-member components, Ak, FAGeh and Geh ($\text{Ca}_2\text{Al}_2\text{SiO}_7$), of the synthetic melilites were $\text{Ca}_{2.015}\text{Mg}_{1.023}\text{Si}_{1.981}\text{O}_7$ (100Ak), $\text{Ca}_{2.017}\text{Mg}_{0.788}\text{Fe}^{3+}_{0.187}\text{Al}_{0.221}\text{Si}_{1.791}\text{O}_7$ (80Ak), $\text{Ca}_{1.995}\text{Mg}_{0.695}\text{Fe}^{3+}_{0.258}\text{Al}_{0.318}\text{Si}_{1.723}\text{O}_7$ (70Ak) and $\text{Ca}_{1.982}\text{Mg}_{0.495}\text{Fe}^{3+}_{0.449}\text{Al}_{0.519}\text{Si}_{1.535}\text{O}_7$ (50Ak), respectively.

The site populations at the T1 and T2 sites were $[0.788\text{Mg}+0.054\text{Fe}^{3+}+0.158\text{Al}]\text{T}_1[0.056\text{Fe}^{3+}+0.153\text{Al}+1.791\text{Si}]\text{T}_2$ for 80Ak, $[0.695\text{Mg}+0.105\text{Fe}^{3+}+0.200\text{Al}]\text{T}_1[0.112\text{Fe}^{3+}+0.165\text{Al}+1.723\text{Si}]\text{T}_2$ for 70Ak and $[0.495\text{Mg}+0.173\text{Fe}^{3+}+0.332\text{Al}]\text{T}_1[0.281\text{Fe}^{3+}+0.153\text{Al}+1.535\text{Si}]\text{T}_2$ for 50Ak (apfu: atoms per formula unit), respectively. The results indicate that Fe^{3+} is distributed at both the T1 and the T2 sites. The mean T1-O distance decreases with the substitution of $\text{Fe}^{3+} + \text{Al}^{3+}$ for Mg^{2+} at the T1 site, whereas the mean T2-O distance increases with substitution of $\text{Fe}^{3+} + \text{Al}^{3+}$ for Si^{4+} 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 Mossbauer and $\text{CuK}_{\alpha 1}$ X-ray line profile analyses. The Mossbauer spectra of the melilites consist of two doublets assigned to Fe^{3+} at the T1 site and two or three doublets to Fe^{3+} at the T2 site, which imply the existence of multiple T1 and T2 sites with different site distortions, respectively. The existence of two T1 sites is not influenced by ionic substitution. Conversely, the splitting of T2 sites becomes more remarkable with the substitution of $\text{Fe}^{3+} + \text{Al}^{3+}$ for Si^{4+} which results in the increase of volume and site distortion of the T_2O_4 -tetrahedra.

Incommensurate structure in melilite has been interpreted rather statically, based on the crystal structure of kermanite, that the incommensurate structure is caused by the misfit between the tetrahedral sheet and the polyhedral sheet. However, as found in this study, effect of ionic substitution at the T1 and T2 sites on the formation of incommensurate structure is also significant. The first factor is the site distortion arising from the distribution of cations with different ionic radii in the T1 and T2 sites. Even though the cation sites are symmetrically equivalent in the average structure, each tetrahedron which is occupied by different cation(s) has variant volume. The second factor is the site distortions caused by the difference of adjacent coordination polyhedra around tetrahedra. Therefore, in Ak-FAGeh melilite solid solutions, the site distortions caused by the ionic substitution at the tetrahedral sites play important role on the formation of the incommensurate structure.

Keywords: synthetic melilite, incommensurate structure, X-ray powder diffraction method, Electron diffraction, Mossbauer spectroscopy